APPLICATION OF STABLE CARBON ISOTOPE ANALYSIS
TO CONTINUOUS COAL/OIL COPROCESSING

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INTRODUCTION

Stable carbon isotope analysis is a promising technique for distinguishing and quantifying the individual contributions of the coal and petroleum feedstocks to coprocessing products. Such information is valuable for process modeling and optimization and for discerning reaction pathways and interactions between the two feedstocks. Carbon isotope analysis provides information only on the fate of carbon; however, this is a minor limitation because most products are 85-90% carbon. A potentially significant obstacle to accurate quantitation is selective isotopic fractionation, a phenomenon by which the two stable carbon isotopes from a single feedstock selectively report to different products. Selective isotopic fraction appears to be exacerbated by reaction severity, and it can cause large quantitation errors at high conversion conditions unless some means is employed to correct for it. This paper describes the isotope analysis of samples from a continuous coprocessing bench-unit run performed by Hydrocarbon Research, Inc. (HRI) with Maya vacuum still bottoms (VSB) and Taiheiyo (Japanese) coal at high conversion conditions. A method to correct for selective isotopic fractionation was employed that allowed quantitation of the conversions of the individual feedstocks.

BACKGROUND

Fifteen product oils and two feedstocks were obtained from S. V. Panvelker, of HRI, from HRI continuous coprocessing bench Run 238-2, also known as Bench Run 4. Run 238-2 was a 25-day feedstock reactivity test performed with Maya VSB and Taiheiyo coal. The run was completed in November 1988. Six sets of operating conditions (1,2), each lasting 4 or 5 days, were used during the run, as illustrated in Table 1. The principal variables were oil to MF coal ratio, space velocity, temperature, and catalyst age. Recycle was used only during the 1/1 oil/coal periods. Product yields (2,3) are reported in Table 2. The product samples obtained included five fractions of the net products from each of periods 5, 13, and 25 (conditions 1, 3, and 6, respectively). The fractions included initial boiling point (IBP) by 350°F, 350 by 650°F, and 650 by 975°F distillates, 975°F+ solubles, and unwashed pressure-filter solids. Samples of the two feedstocks also were obtained. Sample size ranged from 10 to 50 g for each sample. Carbon content was determined on each sample with a LECO CHN-600 instrument. Carbon isotope analyses were performed in duplicate on each sample at the Stable Isotope Laboratory of Conoco Inc. in Ponca City, Oklahoma. Carbon isotope ratios and carbon contents of all samples appear in Table 3. The chemical analysis of the coal appears in Table 4.

DISCUSSION

Through use of the isotope ratios and a simple mixing equation, one can calculate the coal carbon/total carbon ratio of each product. Such an approach assumes that there is no selective fractionation of the isotopes, or at least that it is small

enough to be ignored. Uncorrected results, which appear in Table 5, show an over-accounting of coal carbon, presumably from selective fractionation.

Though gas and insoluble organic matter (IOM) samples were not received for analysis, their delta values and carbon contents can be estimated by forcing carbon and carbon isotope balances to 100%. This was done as follows: The pressure-filter solids (PFS) contain entrained oils (lower half of Table 2). The overall yields were adjusted to include the PFS by substituting the PFS for appropriate amounts of each component in the overall yield. Yields and carbon and isotope analyses were thus available on all products except the gas, which was then forced. With the forced gas data so obtained, the IOM data could be forced. The forcing calculation method is detailed elsewhere (4). Several comments on the results from this exercise, which appear in Table 6, are in order. The forced carbon contents of the gases appear reasonable in light of their composition (Table 2). The negative uncorrected coal carbon contents calculated for the gases merely reflect their light (more negative) isotopic composition. This is to be expected and has been observed in those cases for which gas samples actually were analyzed. Of course, the negative values have no physical meaning; they merely reflect isotopic fractionation. The IOM fractions have quite small yields, reflecting the high coal conversions (ca. 95% MAF). The uncorrected calculated carbon contents of the IOM fractions are not fully reasonable; for example, the Condition 1 IOM has more carbon than total mass. This reflects the combination of all errors. The errors in IOM carbon contents are actually quite small on an absolute basis, being less than 1% in all cases. The uncorrected calculated coal carbon contents of the IOMs indicate that their carbon content is virtually all coal-derived.

As noted, the isotope analyses of the product fractions actually analyzed result in an overabundance of coal carbon when not corrected. This overabundance results from the high yields (15-18%) of isotopically light gases (ca. -30.4 per mil from forced balances). Even though the carbon content of the gases is only about 40 to 50%, they still account for 8 to 9% of the total carbon in the feedstocks. A first-order correction to the data can be applied by assuming that the carbon contained in the gases is formed from the petroleum and coal in proportion to the petroleum carbon and coal carbon in the feedstock. The fraction of the petroleum carbon and coal carbon that is not converted to gas then, has an isotope ratio that is heavier (less negative) than the whole petroleum and coal feeds, respectively. The correction method used here relies on three assumptions: 1) the carbon in the gas is formed from the two feedstocks in proportion to the carbon fed to the unit from each feedstock, 2) the difference between the $\delta^{13}C$ of each feedstock and the $\delta^{13}C$ of the gas produced from that feedstock is the same for the coal and the petroleum, and 3) the non-gas-producing carbon undergoes no further selective isotopic fractionation. The calculation method used to make this correction is detailed elsewhere (4). With this correction approach, we calculate delta values of the non-gas-producing petroleum carbon to be -26.88, -26.82, and -26.80 per mil for Conditions 1, 3 and 6, respectively; the average value is -26.84 ±0.04 per mil. The non-gas-producing coal carbon is calculated to have delta values of -23.75, -23.68, and -23.66 per mil, respectively, for the same periods, with an average delta value of -23.69 ±0.05 per mil. The calculated delta values of the petroleum gas and coal gas average -31.46 and -28.32 per mil, respectively.

Carbon sources, selectivities, and conversions of the non-gaseous products are shown in Table 7 on the basis of the corrected delta values. Selectivity is the enrichment of coal carbon/total carbon in a product relative to the whole feed-stock. Carbon sources are plotted in Figure 1, coal carbon conversions are plotted in Figure 2, and petroleum carbon conversions are plotted in Figure 3. The following observations concern the corrected results from Table 7 and Figures I

through 3. The coal carbon to total carbon ratio in the condensed product fractions increases with boiling point with the one exception of the 975°F+ soluble product. The selectivity data (Table 7) indicate that the IBP x 350°F and 350 x 650°F products are selectively produced from petroleum. The 650 x 975°F and IOM products are selectively produced from coal. The 975°F+ solubles are produced from the two feedstocks without selection. The IOM carbon is close to being entirely coal-derived. In Condition 3, the IOM carbon is calculated to be more than 100% coal-derived; as noted earlier, this error appears to be associated with the need to determine the IOM properties by forced carbon and isotope balances. As expected, all fractions show the greatest coal carbon contributions during Condition 3, which was operated at a 1/1 petroleum/coal ratio. Conditions 1 and 6 were identical (except for catalyst age), including a 2/1 petroleum/coal ratio, and coal carbon contributions are quite similar for their respective products.

The major coal product is the 650 x 975°F distillate (Figure 2); 35 to 42% of the coal carbon reports to that fraction. The coal carbon conversions to IOM (3.4 to 5.8%) indicate that the total conversion of coal carbon to solubles was 94 to 97%. The major petroleum product is the 350 x 650°F distillate (Figure 3); about 38% of the petroleum carbon reports to that fraction. Very little of the petroleum carbon reports to the IOM product.

Interestingly, there is very little difference in conversions of the individual feedstocks between the run periods at petroleum/coal ratios of 2/1 (Conditions 1 and 6) and at 1/1 (Condition 3). Though other operating conditions (T, SV) also were changed, this suggests that within the precision of the data there is no synergy between the feedstocks for conversion, or at least that the degree of synergy is unchanged at ratios of 1/1 and 2/1.

SUMMARY

The analytical results show that selective isotopic fractionation was severe enough during HRI Run 238-2 that accurate carbon source quantitation and individual feedstock conversions cannot be obtained without correcting for isotopic fractionation. A first-order correction was applied that assumes that the feedstocks each fractionate into two "pools" of differing isotopic composition: the gas and the condensed products. The results support the validity of the correction method employed. The petroleum more readily produces light products. Its major product is the 350 x 650°F distillate, whereas that of the coal is the 650 x 975°F distillate. The insoluble organic matter (IOM) is nearly all coal-derived and the naphtha is mostly petroleum-derived. The 975°F+ soluble product is produced in proportion to the feedstock blend. There is no evidence for synergistic interactions between the two feedstocks with respect to conversion to products.

ACKNOWLEDGMENTS

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TABLE 1
OPERATING CONDITIONS: HRI COPROCESSING RUN 238-2

Condition	1	2	3	4	5	6
Period	1-5	6-9	10-13	14-17	18-21	22-25
Oil to MF Coal Ratio	2	1	1	2	2	2
Recycle-to-Fresh-Feed Ratio	0	0.5	0.5	0	0	0
Relative Space Velocity	1	1	1.6	1.6	1.6	1
Temp., °F (1st and 2nd Stage)	810	810	825	825	810	810

Feedstocks: Taiheiyo coal; Maya VSB
Catalysts: Commercial Ni/Mo on alumina, both stages, batch aged during run.
Source: Reference 1, and for temperatures and catalyst, Reference 2.

TABLE 2
PRODUCT YIELDS: HRI COPROCESSING RUN 238-2

Condition	1	2	3	4	5	6
Period	5	8/9	13	-	-	25
Yields, wt % of dry feed						
H_2O, H_2S, NH_3	8.63		9.32	-	-	8.09
CO	0.05	11.0	0.16	-	-	0.06
CO_2	0.03		0.09	-	-	0.05
C_1 x C_3	4.89	5.5	5.18	-	-	3.97
C_4 x C_7 (in gas)	3.52		3.19	-	-	2.97
IBP x 350°F	12.91		12.72	-	-	13.41
350 x 650°F	32.82	34.7	28.53	-	-	31.05
650 x 975°F	26.57	21.2	24.90	-	-	25.96
975°F+ Solubles	9.59	9.2	11.48	- \	-	11.19
IOM	0.88	1.9	1.94	-	-	1.42
Ash	4.27	6.4	6.41	-	-	4.27
H_2 Consumption	-4.16	-4.4	-3.88	-	-	-3.37
Sum(a)	100.00	100.1	100.04	-	-	99.07
Performance, wt % MAF						
Coal Conversion	-	95.6	-	-	-	-
975°F+ Conversion	-	87.5	-	-	-	-
Composition of Unwashed Pressure-Filter Solids, wt % of dry feed						
650°F-	0.10	-	0.41	-	-	0.17
650 x 975°F	1.45	-	3.74	-	-	3.24
975°F+ Solubles	0.63	-	2.11	-	-	1.84
IOM	0.88	1.9	1.94	-	-	1.42
Ash	4.27	6.4	6.41	-	-	4.27
Total	7.33	-	14.62	-	-	10.94

(a) Sums may not equal exactly 100.00% because of slightly different calculation methods used by HRI to arrive at these gas and liquid yields.
Source: Reference 3 and, for Condition 2 data, Reference 2.

TABLE 3
CARBON ISOTOPE RATIOS AND CARBON CONTENTS

	Operating Condition	$\delta^{13}C$, per mil avg.$\pm$std. dev.(b)	Carbon wt % (d)
Feedstocks			
Taiheiyo Coal (HRI #5595)	All	-24.12 $\pm$0.02	68.36(d)
Maya VSB (HRI #5567)	All	-27.26 $\pm$0.02(c)	85.75
Products			
IBP x 350°F	1	-26.50 $\pm$0.01	85.41
350 x 650°F		-26.14 $\pm$0.06	87.38
650 x 975°F		-25.75 $\pm$0.04	87.54
975°F+		-25.88 $\pm$0.01	91.11
Pressure Filter Solid(a)		-25.08 $\pm$0.14	47.96
IBP x 350°F	3	-25.70 $\pm$0.03	85.10
350 x 650°F		-25.70 $\pm$0.06	87.76
650 x 975°F		-24.98 $\pm$0.11	88.10
975°F+		-25.54 $\pm$0.01	89.57
Pressure Filter Solid(a)		-24.84 $\pm$0.09	47.06
IBP x 350°F	6	-26.29 $\pm$0.03	85.77
350 x 650°F		-26.19 $\pm$0.07	87.32
650 x 975°F		-25.51 $\pm$0.01	88.01
975°F+		-25.90 $\pm$0.06	91.18
Pressure Filter Solid(a)		-25.42 $\pm$0.01	51.09

(a) Unwashed.
(b) All isotope analyses performed in duplicate at Conoco's Stable Isotope lab.
(c) Original duplicate set of analyses gave -26.20 and -26.86 per mil; however, analyst noted that he could not obtain a representative sample for that pair of analyses. Repeat duplicate analysis are shown.
(d) Reported on an as-determined basis for all samples, except for coal which is reported on a MF basis.

TABLE 4
ANALYSIS OF TAIHEIYO COAL

Moisture, wt % as determined	4.59
Proximate, wt % dry basis	
Volatile Matter	49.26
Fixed Carbon	38.60
Ash	12.14
Ultimate, wt % dry basis	
C	68.36
H	5.69
N	1.02
O (diff)	12.50
S, total	0.27
pyritic	0.07
sulfate	<0.01
organic (diff)	0.20
Cl	0.019
Ash	12.14
Gross Cal. Value, dry, Btu/lb	12,239

TABLE 5

UNCORRECTED COAL CARBON AS PERCENT OF TOTAL CARBON
HRI COPROCESSING RUN 238-2

Product	Operating Condition	Coal Carbon/ Total Carbon, %(b)
IBP x 350°F	1	24.2 ±0.6
350 x 650°F		35.7 ±2.0
650 x 975°F		48.1 ±1.4
975°F+		44.0 ±0.6
Pressure Filter Solid(a)	↓	69.4 ±4.5
IBP x 350°F	3	49.7 ±1.1
350 x 650°F		49.7 ±2.0
650 x 975°F		72.6 ±3.5
975°F+		54.8 ±0.6
Pressure Filter Solid(a)	↓	77.1 ±2.9
IBP x 350°F	6	30.9 ±1.1
350 x 650°F		34.1 ±2.3
650 x 975°F		55.7 ±0.6
975°F+		43.3 ±2.0
Pressure Filter Solid(a)	↓	58.6 ±0.6

(a) Unwashed.
(b) Standard deviation reflects random error but not bias errors.

TABLE 6

PROPERTIES OF GASES AND IOM PRODUCTS BASED ON MASS, CARBON, AND ISOTOPE BALANCES: HRI COPROCESSING RUN 238-2

Run Condition	Yield, lbs Product/ 100 lbs Dry Feed	lbs Carbon in Product/ 100 lbs Dry Feed	lbs Coal Carbon in Product/ 100 lbs Dry Feed (Uncorrected)	Coal Carbon/ Total Carbon Ratio (Uncorrected)	$\delta^{13}C$, per mil
Hypothetical Gases					
1	17.12	6.66	-6.68	-100.25	-30.41
3	17.94	7.64	-6.89	- 90.20	-30.09
6	15.14	7.37	-8.06	-109.36	-30.69
Hypothetical IOM					
1	0.88	1.58	1.55	97.61	-24.20
3	1.94	1.34	1.70	126.98	-23.27
6	1.42	0.91	0.91	99.71	-24.13

TABLE 7
CORRECTED CARBON SOURCES, SELECTIVITIES AND CONVERSIONS
HRI COPROCESSING RUN 238-2

Product	Run Condi- tion	Coal Carbon as a % of Total Carbon (a)	Selectivity for Coal Carbon (b)	Conversion of Coal C to Fraction, %	Conversion of Petroleum C to Fraction, %
Hypothetical Gas	1	28.5	1.0	8.3	8.3
IBP x 350°F		10.8	0.4	5.2	17.2
350 x 650°F		22.2	0.8	28.0	39.0
650 x 975°F		34.6	1.2	35.3	26.6
975°F⁺ Solubles		30.5	1.1	11.7	10.6
Hypothetical IOM		83.8	2.9	5.8	0.4
Total		-	-	94.3	102.1
Hypothetical Gas	3	44.4	1.0	9.9	10.0
IBP x 350°F		36.9	0.8	11.7	15.9
350 x 650°F		36.9	0.8	27.0	36.8
650 x 975°F		60.2	1.4	38.6	20.4
975°F⁺ Solubles		42.1	0.9	12.7	13.9
Hypothetical IOM		115.8	2.6	4.5	0.5
Total		-	-	104.4	96.5
Hypothetical Gas	6	28.5	1.0	9.2	9.2
IBP x 350°F		17.5	0.6	8.8	16.6
350 x 650°F		20.6	0.7	24.6	37.7
650 x 975°F		42.2	1.5	42.3	23.1
975°F⁺ Solubles		29.8	1.0	13.4	12.5
Hypothetical IOM		86.0	3.0	3.4	0.2
Total		-	-	101.7	99.3

(a) Petroleum carbon as % of total carbon is 100% minus this value.
(b) Selectivity is calculated as the ratio of coal carbon/total carbon in a product fraction to the coal carbon/total carbon ratio in the whole feedstock.
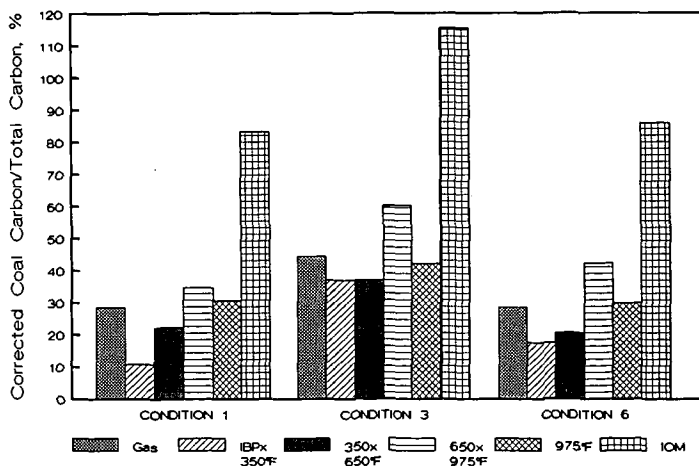

Figure 1. Corrected Coal Carbon to Total Carbon Ratios Plotted vs Run Condition. HRI Run 238-2.
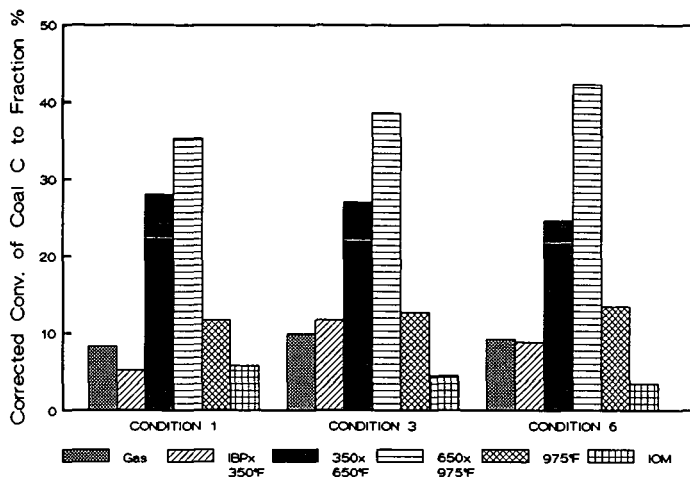
Figure 2. Corrected Conversions of Coal Carbon Plotted
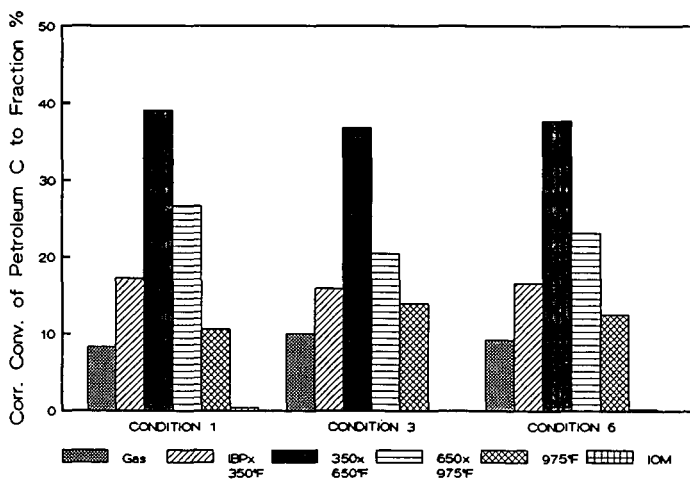vs Run Condition. HRI Run 238-2.

Figure 3. Corrected Conversions of Petroleum Carbon Plotted
vs Run Condition. HRI Run 238-2.

PHASE SPLITTING AND SYNERGISM IN COAL OIL COPROCESSING AND COAL LIQUEFACTION

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ABSTRACT

The phase behaviour of complex hydrocarbon systems relevant to coal-oil coprocessing and direct coal liquefaction was investigated in the temperature range 600 to 700 K, using a batch autoclave apparatus. Bitumen and heavy oil + anthracene mixtures as well as model liquefaction solvents such as pyrene + tetralin are shown to exhibit phase splitting in this region. Gas phase constituents such as H_2, N_2, CH_4, C_2H_6 were found to influence the size and shape of the phase splitting zone but did not alter the phase behaviour per se. Significant fluctuations in the light oil yield obtained from laboratory and pilot scale models of coal/oil coprocessing and direct coal liquefaction processes are frequently attributed to synergism. In this paper, some aspects of synergism are related to phase splitting and the influence of phase splitting on reaction schemes. Preliminary criteria for solvent/diluent selection and operating conditions are proposed.

KEY WORDS: coprocessing, coal liquefaction, synergism

INTRODUCTION

Kinetic studies in heavy oil upgrading, coal/oil coprocessing and direct coal liquefaction are frequently conducted without due consideration for the physical properties of solvents or diluents under the reaction conditions employed (650 to 750 K, 4 to 30 MPa). Consequently, significant fluctuations in light oil yields obtained from laboratory and pilot scale studies, arising from apparently minor perturbations in operating conditions, are frequently attributed to synergistic phenomena [1-6]. As the reaction conditions associated with coprocessing and coal liquefaction typically intersect the critical region of one or more of the principal liquid constituents [7], complex phase behaviour can be anticipated [8, 9]. Phase splitting, for example, is a common phenomenon in the critical and subcritical regions [10]. In addition, hydrogen is a principal reagent in both coal dissolution [11] and oil hydrogenation reactions and hydrogen solubility in liquids is sensitive to composition [12]. Phase splitting and hydrogen solubility can have a direct and significant impact on observed rates for coal dissolution reactions [13, 14], for example, and these phenomena provide a satisfactory explanation for 20 wt % fluctuations in coal conversion arising in pyrene-tetralin mixtures under hydrogen [15] which had previously been attributed to synergism [1]. Results obtained by Rincon and Angulo [3, 4] and Fouda et al. [6] are also consistent with phase splitting [16]. The transition of the diluent or solvent from liquid to supercritical fluid is another phenomenon which can have a significant impact on reaction kinetics.

Many of the model compounds and liquids employed are unstable under the operating conditions investigated and the phase data presented are not equilibrium data per se. Catalysts are ubiquitous actors in these systems and their effect can only be minimized. Glass liners reduce the impact of trace pyrrhotite (a well known dehydrogenation catalyst) on reactor walls, but do not prevent catalytic hydrogenation due to catechol adsorption on stirrer surfaces [17]. Homogeneous isomerization, pyrolysis, and other reactions cannot be neglected at elevated temperatures. The degradation of pyrene [2, 15] and tetralin [18-21], for example, has been reported. Compound degradation cannot be ignored or prevented and phase compositions inevitably exhibit a time dependence.

EXPERIMENTAL

Experiments were conducted in a glass lined PPI autoclave having an inside diameter of 0.095 m and 0.3 m long. The autoclave, equipped with magnetically driven stirrer, internal cooling coil and three heated sample ports, was placed vertically in a 3000 W muffle furnace. All apparatus components were fabricated from type 316 stainless steel. The autoclave temperature was maintained within two degrees of a set point using an Athena temperature controller and a manually actuated internal cooling coil. All model compounds were reagent grade and supplied by Fluka. The anthracene oil was supplied by Allied-Signal and Athabasca bitumen and Venezuela heavy oil vacuum bottoms were supplied by CANMET. Their

properties are listed in Table 1. After loading the autoclave with 150 g of liquid, air was removed by flushing and the autoclave was charged with hydrogen, methane, etc. to a preset pressure and heated at 6 K min⁻¹ to the first set point. Once the temperature reached the set point, operating parameters were fixed for 0.5 h. Agitation facilitated the acquisition of phase data. However, it proved necessary to cease agitation 0.5 h before sample retrieval so that emulsions, if present, could break [15]. Samples were collected in ice cold sample vials and immediately diluted in toluene. Species that did not condense at 273 K were not collected. Following sample retrieval the autoclave was heated to subsequent set points and the procedure was repeated.

Samples were analyzed chromatographically and mass spectra were obtained using a Hewlett Packard 5987A radio frequency quadrupole mass spectrometer. Many peaks were not identified unambiguously. Samples (1 μl) were injected directly into a 30 m DB-17 column. Column operating conditions were: carrier gas, helium; temperature program, 373 K for three minutes, 373-548 K at 20 K min⁻¹. Additional GCMS analysis and ASTM standard boiling point data were provided by Shell Canada Ltd. Compositions are repeatable to within 2 to 3 mole %.

RESULTS AND DISCUSSION

Partial phase diagrams for the model systems pyrene + tetralin + (ethane, no gas, nitrogen, or methane) are shown in Figures 1 through 3 respectively. At low gas pressures a liquid-liquid zone appears in all cases at temperatures exceeding 640 K. This zone grows with temperature and at 698 K is quite broad eg. the zone is bounded by 0.25 and 0.60 mole % pyrene when no gas is added. Only ethane causes this zone to shrink at elevated temperatures Figure 1a. Phase splitting can also arise at elevated pressures. For example, with nitrogen (Figure 2), phase splitting arises from splitting of the liquid phase. The high pressure and low pressure zones combines at elevated temperatures. With methane, Figure 3, the vapour phase splits at elevated pressures but these two phases do not coexist with a third phase. Key transitions arising in these systems include: gas-liquid to gas-liquid-liquid at low or high pressure, gas-liquid-liquid to gas-liquid, fluid-fluid or fluid at elevated pressures. These systems are most susceptible to phase splitting at low pyrene contents.

Dukhedin-Lalla et al. [16] reported that the model solvent system indene-decalin did not undergo phase splitting and that the synergism observed by Chiba et al. [2] could not be explained by phase splitting of solvent components. However, decalin is unstable in mixtures with indene, or indene + anthracene oil, as shown in Table 2, and forms naphthalene or naphthalene derivatives at elevated temperatures. The solubility of pyrene like coal liquids in naphthalene at 673 K is 15 to 20 wt % depending on pressure and gas composition as shown in Figures 1 through 4. Chiba et al. [2] reported coal conversions of 53, 65, and 35 wt % in indene, indene (50 wt %) + decalin, and decalin at this temperature and attributed the fluctuation to synergism. The corresponding concentrations of the coal derived liquids in the solvents are 18, 22, and 13 wt %. These concentration values are based on the initial charges of coal (6 g) and solvent (18 g), to a 0.1 litre reactor and the physical properties of naphthalene. The impact of solvent expansion, and evaporation was included in the calculations. While the operating conditions and compositions for the pbase and liquefaction experiments were not identical, the conversion of coal in "decalin", which corresponds to a coal derived liquid concentration in the solvent of 13 wt % compares favourably with the solubility limit for pyrene in naphthalene. The coal conversions reported by Chiba et al. [2] are consistent with phase splitting resulting from exceeding the solubility of coal derived liquids in the solvent where the solubility limit is a function of solvent composition. The decrease in coal conversion in solvents with a high "decalin" content can be explained in a manner analogous to the explanation of synergism in the pyrene-tetralin solvent system [15].

Complex mixtures of aliphatic and aromatic compounds also exhibit phase splitting as shown in Figure 4. Venezuela vacuum bottoms + anthracene oil and Athabasca bitumen + anthracene oil mixtures both exhibit phase splitting above 640 K for compositions in the 30 to 70 wt % range. As many of the species present could not be identified unambiguously or were retained by the column, the compositions shown in figure 4 are incomplete. Simple model systems do not mimic the behaviour of complex systems in this case. Pyrene-hexadecane mixtures, for example, only begin to phase split at 698 K for pyrene contents in excess of 75 wt %. Curtis et al. [5] reported coal conversions for a series of experiments which simulate the transition from coprocessing to coal liquefaction with complex solvents. The solvents comprised mixtures of Maya TLR (petroleum based) and V1067 (a bottoms recycle solvent from the

Wilsonville coal research facility). The authors showed that coal conversion decreased slightly, from 65 to 60 wt %, at 698 K as the V1067 content of the solvent increased from 0 to 35 wt %, with a large coincident increase in insoluble organic matter derived from the solvent. Then coal conversion began to increase rapidly to 75 and 90 wt % conversion at solvent compositions of 50 and 100 wt % V1067. The coal derived liquid content at the end of each of these experiments is 25, 50, 64, and 100 wt % respectively. These results are also consistent with phase splitting. The coal derived liquid content in the experiment where Maya TLR was used as a solvent is 25 wt %. Our results show that at 30 wt % mixtures of coal liquids and petroleum feed stocks phase split. So adding coal liquids to the solvent saturates the solvent with coal liquid thus inhibiting coal dissolution. A separate dispersed liquid phase is is then formed which leads to an increase in the production of insoluble organic matter (IOM) as the dispersed liquid becomes hydrogen starved due to poor liquid-liquid mass transfer and polymerization reactions dominate in this phase. If sufficient coal liquid is added to the solvent it becomes the continuous liquid phase and there is a sharp increase in coal solubility at this point because it is more soluble in coal derived solvent than in petroleum derived solvent. Consequently a greater fraction of the coal is solubilized and hydrogenated, coal conversion increases and the IOM produced by the coal based solvent decreases. In this case the continuous phase appears to change over at a coal liquid content of approximately 50 wt %.

Phase splitting is a fundamental characteristic of the coprocessing and coal liquefaction reaction environment and cannot be neglected in the design or interpretation of experiments, or the design of processes. In coprocessing, for example, care must be taken to ensure that the anticipated coal derived liquid concentration in the diluent does not exceed the solubility limit. Extant data [5, 6] and the present work place the solubility limit in the 25 to 30 wt % range but more dilute systems are preferred. Coal liquids exhibit phase splitting between 2 and 4 ringed compounds. Thus, in direct coal liquefaction, two optima appear to exist from the point of view of solvent selection which lead to different reactor design choices:
1. a heavy recycle solvent operated at a pressure sufficient to ensure adequate hydrogen availability,
2. a middle distillate operated at a pressure high enough to avoid the phase split zone.
The first optimum is best exemplified by the so-called German technologies whereas the second optimum has received little attention [22].

CONCLUSIONS

Phase splitting has been shown to arise in both simple and complex mixtures of aromatic, polynuclear aromatic and aliphatic compounds. This phenomenon is shown to account for fluctuations in coal conversions arising in coal oil coprocessing and coal liquefaction previously attributed to synergism. In particular, liquid yields from coal in coprocessing appear to be limited by the solubility of coal liquids in petroleum based solvents. In coal liquefaction the situation is more complex and a minimum of two solvent optima exist.

ACKNOWLEDGEMENTS

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TABLE 1: Physical Properties and Compositions of Oils (wt %)

		Anthracene Oil	Athabasca Bitumen	Venezuela (blend 24)
Specific gravity		(288.5 K) 1.092	(297 K) 1.046	(294 K) 1.026
Water, %		0.2	-	-
Xylene insoluble, %		0.08	-	-
Pentane insoluble, %		-	38.4	21.4
Distillation, % to	498 K	0.0	-	-
	543 K	7.9	-	-
	588 K	43.7	-	-
	628 K	80.5	-	-
	+628 K	19.0	-	-
	+798 K	-	99.3	95.1
Elemental analysis	C		84.3	84.3
	H		10.9	9.6
	N		0.8	0.7
	O		0.3	0.7
	S		3.5	6.0
Aromatic carbon, %			35.4	30.0
Mean molar mass			983	848

COMPOUND (MOLE FRACTION)		648 K			673 K			698 K		
		PORT 1	PORT 2	PORT 3	PORT 1	PORT 2	PORT 3	PORT 1	PORT 2	PORT 3
INDENE or BENZENE derivative	C_9H_{12}	0.641	0.556	0.533	0.542	0.543	0.269	0.269	0.224	0.205
DECALIN (cis & trans)	$C_{10}H_{18}$	0.186	0.181	0.171	0.039	0.116	0.031	0.000	0.000	0.000
INDENE or BENZENE derivative	$C_{10}H_{12}$	0.000	0.014	0.016	0.023	0.013	0.000	0.000	0.000	0.000
SPIRO (4,5) DECANE	$C_{11}H_{?}$	0.030	0.033	0.035	0.000	0.015	0.000	0.000	0.000	0.000
TETRALIN	$C_{10}H_{12}$	0.000	0.031	0.012	0.010	0.000	0.000	0.000	0.000	0.000
NAPHTHALENE	$C_{10}H_8$	0.073	0.091	0.119	0.229	0.171	0.450	0.575	0.584	0.608
NAPHTHALENE derivative	$C_{11}H_{10}$	0.011	0.013	0.018	0.032	0.021	0.046	0.040	0.050	0.034
NAPHTHALENE derivative	$C_{12}H_{12}$	0.000	0.000	0.000	0.022	0.000	0.000	0.000	0.000	0.000
ACENAPHTHENE	$C_{12}H_{10}$	0.017	0.028	0.028	0.016	0.023	0.000	0.000	0.000	0.000
DIBENZOFURAN	$C_{12}H_8O$	0.009	0.018	0.013	0.019	0.023	0.039	0.000	0.032	0.000
9-H FLUORENE	$C_{13}H_{10}$	0.011	0.024	0.015	0.030	0.030	0.053	0.036	0.033	0.053
DIBENZOFURAN derivative	$C_{13}H_{10}O$	0.000	0.002	0.002	0.000	0.000	0.000	0.000	0.000	0.000
ANTHRACENE	$C_{14}H_{10}$	0.021	0.017	0.031	0.024	0.028	0.061	0.080	0.035	0.058
PYRENE or FLUORANTHENE	$C_{16}H_{10}$	0.000	0.012	0.008	0.015	0.016	0.051	0.000	0.042	0.018
2 RINGED		0.941	0.899	0.903	0.896	0.879	0.796	0.884	0.858	0.847
3 RINGED		0.058	0.089	0.089	0.089	0.104	0.153	0.116	0.100	0.111
4 RINGED		0.000	0.012	0.008	0.015	0.016	0.051	0.000	0.042	0.041

PYRENE – TETRALIN with 3.5 MPa ETHANE

PYRENE – TETRALIN with 0 MPa initial pressure
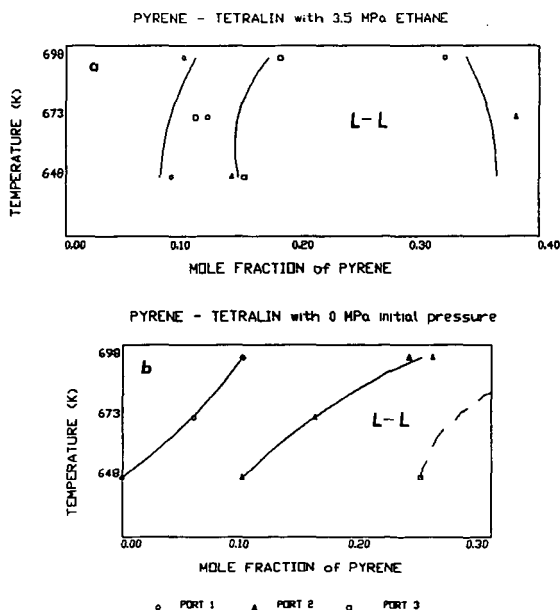
○ PORT 1   ▲ PORT 2   □ PORT 3

FIGURE 1: Partial phase diagrams for the systems pyrene + tetralin + ethane (a), and pyrene + tetralin (b)
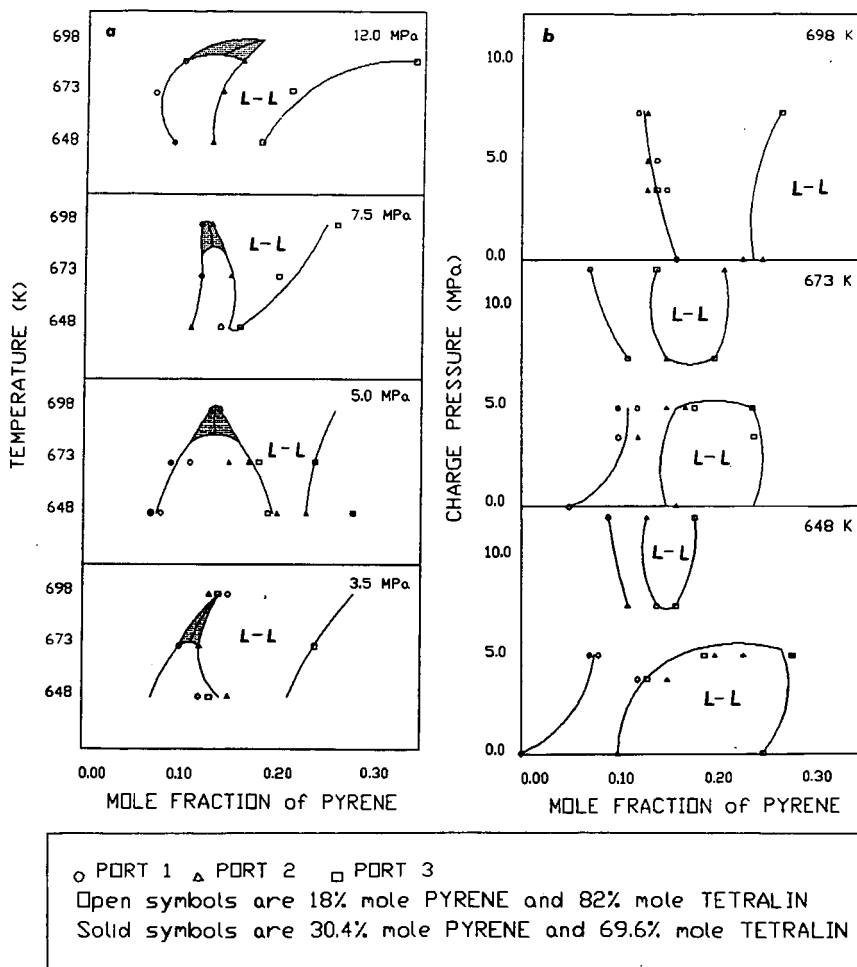
FIGURE 2: Partial phase diagram for the system pyrene + tetralin + nitrogen showing isobars (a) and isotherms (b)
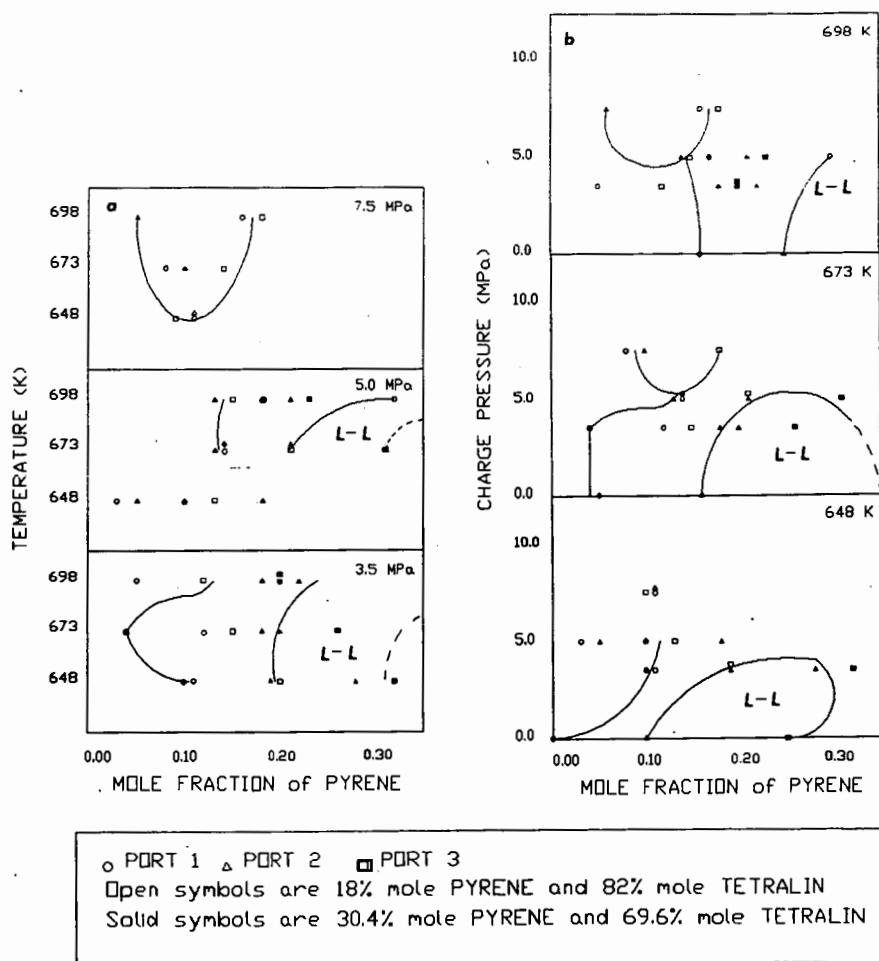
FIGURE 3: Partial phase diagram for the system pyrene + tetralin + methane showing isobars (a) and isotherms (b)
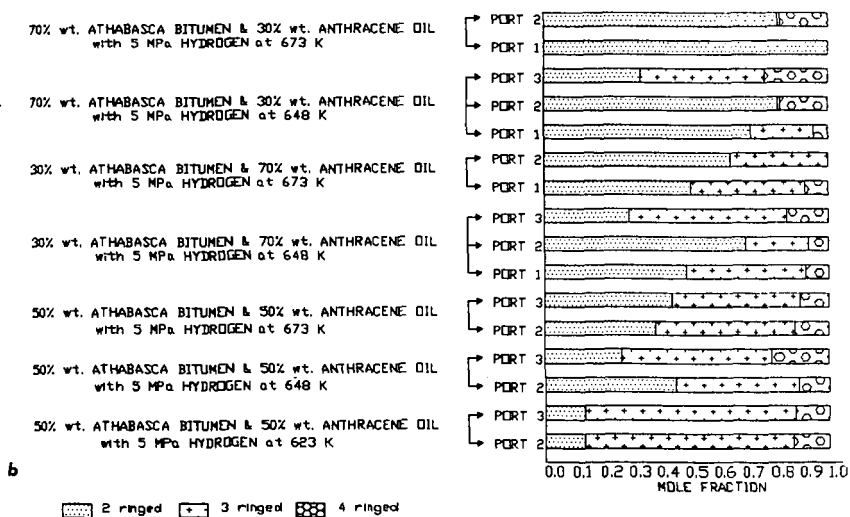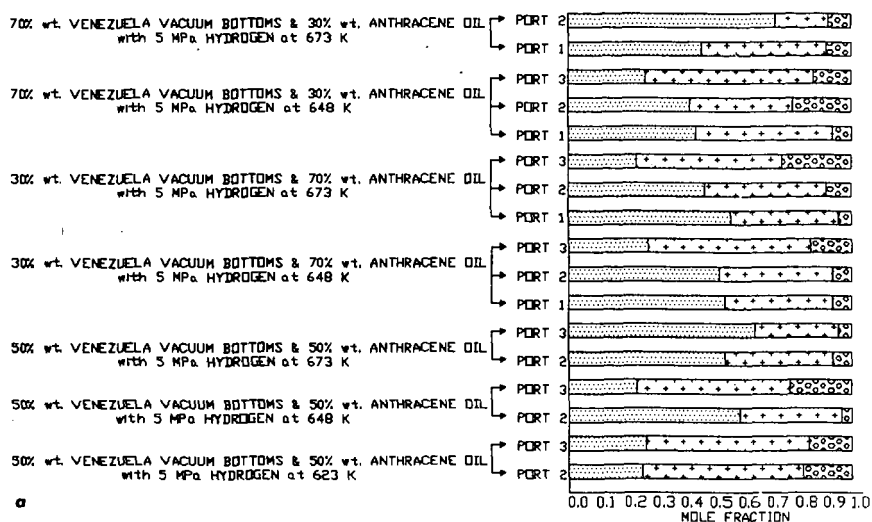
FIGURE 4: Sample compositions obtained from ports located at the top (1) middle (2) and bottom (3) of the reactor for Venezuela vacuum bottoms + anthracene oil + hydrogen mixtures (a), and Athabasca bitumen + anthracene oil + hydrogen mixtures (b)

CHARACTERIZATION OF SOLIDS FROM COAL/RESID COPROCESSING

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ABSTRACT

Solids formed from coprocessing of 10% coal/90% resid were characterized by
solvent extraction, elemental analyses, C^{13}/C^{12} isotope ratio, ESR, and GPC
techniques. The total solids obtained from filtration contained at least 60%
adsorbed petroleum—derived material (oil, resin, asphaltene). The THF insolubles
in the product contained high oxygen, low vanadium and a higher level of
polyaromatic radicals than the soluble fraction, indicating that these insolubles
were largely coal—derived material. However, the fraction of the solid product
that could be dissolved in either THF or pyridine was mostly petroleum—derived.

INTRODUCTION

The background technology of the coprocessing of coal/petroleum resids has been
reviewed by Oelert (1), and additional citations have been discussed in our
companion paper (2) being presented at this conference. In summary, such
coprocessing is done with the goals of providing the addition of a low cost
feedstock, coal; improving unit operability by a reduction in petroleum—derived
coke solids; enhancing metals and heteroatom removal; and reducing hydrogen
requirements relative to direct coal liquefaction.

Our other paper reported on the coprocessing of 10% Illinois No. 6 coal with 90%
resid with decanted oil (DCO) over equilibrium hydrotreating catalyst in a flow
unit at 780°F. The addition of coal considerably increased the yield of solids
obtained from a Shell hot filtration test, SHFT (2), as seen in Table I.

Normally, in resid hydroprocessing, SHFT solids are free of asphaltenes. The
petroleum asphaltene concentration in the product of resid hydroprocessing is
calculated as the difference between hexane insolubles and SHFT solids. For the
resid/DCO experiment shown in Table I, the asphaltene level is 8.2 wt%. The
asphaltene content of the coal/resid/DCO run in Table I calculated in the same
manner is lower, 5.2 wt%. If the same levels of petroleum—derived asphaltenes are
being formed in both cases, a reasonable assumption (although not certain), the
SHFT solids obtained from coal/resid coprocessing must include some petroleum
asphaltenes. Therefore, the use of SHFT solids to define asphaltene yield is not
valid for the coal/resid case. Moreover, material balance analysis indicated that
in addition to asphaltenes, a considerable amount of oil and resin was adsorbed by
the unconverted coal.

The objective of this study was to characterize the solids from the coprocessing
of coal and resid/DCO. This included verifying the presence of adsorbed
petroleum—derived material in the solids; determining the relative distribution of
coal—derived and resid—derived fractions; and characterizing the adsorbed
petroleum—derived material.

EXPERIMENTAL

Reaction Conditions. The coprocessing of 10% Illinois No. 6 with 90% resid with
DCO was conducted in an upflow high—pressure unit which contains two 1—liter
Autoclave reactors in series. Catalyst baskets, each filled with 60 cc of
equilibrium hydrotreating catalyst, were placed in both reactors. To prevent
elutriation, the catalyst was covered with 10 cc of 3 mm glass balls and 1/4 inch

of glass wool. The experiment was conducted at reactor temperatures of 780°F, average feed rate of 206 g/hr and 2500 psig H_2 at 7700 SCFB.

Product Filtration. In addition to the standard SHFT solids determination (2), a modified procedure was used as follows. A composite product was made by blending portions of the daily product samples collected over the 180 hours of coprocessing. This composite product was filtered, the solids were washed with a mixture of 10% toluene and 90% hexane, and then dried in a vacuum oven at 110°C for 16 hours.

Solubility Fractionation. The solids recovered from the above filtration of composite product were sequentially extracted with toluene followed by THF to separate the different solubility fractions. The schematic of the extraction procedure is shown in Figure 1.

Product Analysis. The extracted solubility fractions were analyzed for elemental composition (C,H,N,S,O), metals content (Ni,V) using inductively coupled plasma spectroscopy (ICP), molecular weight distribution using gel permeation chromatography (GPC), and relative levels of polyaromatic radicals and vanadium concentrations using electron spin resonance spectroscopy (ESR). In addition to conventional hexane precipitation, the extracts were separated into oils, resins, asphaltenes and preasphaltenes using a chromatographic technique (3). Oils were eluted from silica gel by hexane; resins were eluted from silica gel by diethyl ether/ethanol (10/1 volume ratio). Asphaltenes and preasphaltenes were insolubles that did not get passed over the silica gel; asphaltenes were toluene soluble (TS), and preasphaltenes were THF soluble and toluene insoluble (THFS/TI). Preasphaltene extraction was also done with pyridine in one case to provide a comparison with THF extraction results.

RESULTS AND DISCUSSION

A mixture of 90% resid and 10% DCO was hydroprocessed for 120 hours, followed by a run period of 180 hours with an added 10% coal. The THF insolubles during the resid/DCO period averaged 0.6 wt%. This value was 3.3 wt% during the coal/resid/DCO period. Therefore, the level of coal conversion to THF solubles was about 80%, assuming no additional THF insolubles were formed from the petroleum-derived feeds during the period of coal addition. This value is lower than the coal conversion results reported by Wilsonville using a similar coal and a coal-derived recycle solvent (4), rather than petroleum liquids. However, due to the low coal feed concentration and the accuracy of the THF insolubles determination, it is not possible to ascertain whether this low conversion is due to solvent effectiveness or to solids being formed from the petroleum feeds.

The SHFT solids during the resid/DCO period averaged 2.3 wt%. This value was 9.6 wt% during the coal/resid/DCO period. The SHFT solids from resid/DCO and coal/resid/DCO hydroprocessing were analyzed for C^{13}/C^{12} concentration ratios using mass spectrometry to determine the relative amounts of coal-derived (or resid-derived) carbon in the SHFT solids. The analyses were performed by Global Geochemistry Corporation in Canoga Park, CA and it was assumed that there was no selective fractionation of the isotopes. The analysis on the SHFT solids indicated that only 28.0% of the solids was coal-derived. Therefore, 6.9% (absolute) was derived from the petroleum fractions, substantially more than the insolubles observed formed without coal present.

The feed coal and the modified SHFT solids from the coal/resid/DCO coprocessing were sequentially extracted with toluene followed by THF to separate different solubility fractions. Table II shows the yields of the solubility fractions from these solids and from the feed coal. The analysis of each of the soluble fractions from the modified SHFT solids for group type is shown in Table III; also shown is the analysis of the resid feed. The relative levels of radical concentrations and vanadium content (paramagnetic VO^{+2}) in selected group types in

each of the solubility fractions were determined from ESR and are shown in Table IV. The elemental composition and metals content (as determined by ICP) of the solubility fractions from the modified SHFT solids are shown in Table V (also shown are the compositions for the coprocessing feed and for the product filtrate). The molecular weight distributions of the toluene soluble fraction (TS) of the coal feed, resid/DCO feed, TS of the modified SHFT solids, and preasphaltenes (THFS/TI) of the modified SHFT solids are shown in Figures 2a,b,c and d, respectively.

Unconverted Coal and THF Insolubles. As shown in Table II, the solids recovered from the filtration of composite product with hexane/toluene (90/10) wash and then THF contained 30 wt% THF insolubles (THFI). If the hexane/toluene wash did not affect the results of the subsequent THF extraction, the THF insolubles (as determined from this sequential extraction) is 2.9 wt% of the product. This value is within the experimental error of 3.3 wt% THF insolubles measured experimentally for the total coal/resid/DCO coprocessing product. Of the 3.3 wt%, 0.6 wt% is resid-derived so that the coal-derived THF insolubles is 2.7 wt%. This value is the same as the 2.7 wt% coal-derived solids inferred from the C^{13}/C^{12} isotope ratio analysis of the SHFT solids.

The high oxygen (Table V) and low vanadium content (Table IV) of the insolubles (THFI fraction) confirm that this is largely coal-derived material. Moreover, these insolubles contain a higher level of free radicals (Table IV) than the asphaltenes in the THF solubles material.

Analysis of the THF Soluble Fractions. The materials retained in the modified SHFT solids were primarily oils and resins, as shown in Table III. The THF solubles of the modified SHFT solids from the coal/resid/DCO run consisted of the toluene solubles and the preasphaltenes; it contained 36 wt% oils, 43% resins and only 21% asphaltenes+preasphaltenes (Table III). The recovered toluene soluble fraction contained 36% oils, 49% resins, and 10% asphaltenes; the remainder of this fraction was made up of preasphaltenes that formed as a result of the extraction and recovery process. The preasphaltene fraction was only about 8% of the modified SHFT solids.

The toluene soluble fraction of these modified SHFT solids was primarily petroleum-derived while the preasphaltenes were a mixture of petroleum- and coal-derived material. The low oxygen content (Table V) and molecular weight distribution (Figure 2b vs. Figure 2c) of the TS confirm that this material is mostly petroleum-derived. In addition, this toluene soluble material had an oil fraction which was very low in radical level (Table IV).

The preasphaltenes retained in the modified SHFT solids definitely had a coal component, as indicated by a high oxygen content (Table V) and the peak in the molecular weight distribution of an estimated value of 250 (Figure 2a vs. Figure 2d). Moreover, the resin fraction of these preasphaltenes contained more radicals than the resin fraction of the TS material (Table IV). These preasphaltenes also had a petroleum contribution, as indicated by its high metals content (Table V). The resin fraction of these preasphaltenes contained six times more vanadium (150 ppm) than the resin fraction of the toluene soluble material (25 ppm). Based on oxygen content, it is estimated that about 24% of the preasphaltenes was coal-derived.

The distribution of free radicals (of polyaromatic nature) among the group types (Table IV) confirms the above observations. Specifically, the free radical level in the asphaltenes is 68% that of the preasphaltenes in the modified SHFT solids. This would be expected if the level of coal-derived material was greater in the preasphaltenes. As a further test, pyridine extraction of the solids was carried out to obtain a pyridine soluble fraction. Pyridine as a more polar solvent extracted twice the level of free radicals than THF; this confirmed that part of the preasphaltenes was coal-derived. The pyridine-extracted preasphaltenes also

contained 20% more vanadium than the THF-extracted preasphaltenes, confirming the petroleum origin of the preasphaltenes.

The characteristics of the toluene soluble material extracted from the modified SHFT solids is shown in Table IV, along with those of the product filtrate and the coprocessing feed. This adsorbed petroleum-derived material had intermediate levels of sulfur, nitrogen and oxygen when compared to the product filtrate and the feed. Metal content was about the same as that of the filtrate and the H/C ratio was comparable to that of the feed. Therefore, this material, 21% of which is 1000°F⁻, is possible additional liquid yield. There is a potential that some of the retained oils and part of the resins could be recovered in a vacuum tower during normal refinery processing.

SUMMARY AND CONCLUSIONS

The THF insolubles and the SHFT solids formed from the coprocessing of 10% Illinois No. 6 coal with a 90/10 resid/DCO feed at 780°F were characterized by solvent extraction, C^{13}/C^{12} isotope ratio, elemental analysis, ESR and GPC. The THF insolubles in these solids contained high oxygen, low vanadium, and a higher level of free radicals than the soluble fraction, indicating that these insolubles were largely coal and coal-derived material. In the characterization of SHFT solids, we found that material containing 36% oils, 43% resins, and 21% asphaltenes and preasphaltenes were retained. The toluene soluble fraction of the SHFT solids was petroleum-derived; and the preasphaltenes were of both coal and petroleum origins. The toluene soluble fraction of the SHFT solids had an intermediate quality between that of the feed and the product filtrate. This represents possible additional liquid yield.

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TABLE I. SOLIDS FROM HYDROPROCESSING AT 780 °F

	YIELD, wt% of feed	
FEED	RESID/DCO	COAL/RESID/DCO
THF Insolubles	0.6	3.3
Hexane Insolubles	10.5	14.8
SHFT Solids	2.3	9.6
Coal-derived SHFT Solids[1]	0.0	2.7

[1] C^{13}/C^{12} isotope analysis on SHFT solids indicated 28.0±5.8% of the solids was coal-derived.

TABLE II. YIELDS OF SOLUBILITY FRACTIONS

	EXTRACTION YIELD, wt%	
FRACTION	MODIFIED SHFT SOLIDS[1]	ILLINOIS NO. 6 (MF BASIS)[2]
Toluene Solubles	62.5	0.6
Preasphaltenes (THF Soluble/ Toluene Insoluble)	7.6	1.8
THF Insolubles (THFI)	29.9	97.6[3]

[1] 9.6 wt% of coprocessing feed (assuming hexane/toluene wash modification to the SHFT test had no effect)
[2] Coal moisture content of 7.1 wt%; coal ash content of 11.5 wt% MF coal.
[3] THF extraction on coal gave 98.0 wt% MF coal.

TABLE III. GROUP TYPE ANALYSIS OF RESID FEED
AND LIQUIDS FROM EXTRACTION OF MODIFIED SHFT SOLIDS

	DISTRIBUTION, wt% of fraction				
FRACTION	OIL	RESIN	ASPHALTENE	PRE-ASPHALTENE	LOSSES
Toluene Soluble	35.7	48.6	9.9	3.3	2.5
THF Soluble	36.0	43.1	10.5	10.4	0.0
Resid Feed	8.6	68.1	20.1	3.2	0.0

TABLE IV. RESULTS OF ESR ANALYSIS ON GROUP TYPES EXTRACTED FROM
THE MODIFIED SHFT SOLIDS

	Relative Radical Concentration	Vanadium (ppm)
Toluene Soluble Oil	1	<0.1
Toluene Soluble Resin	500	25
Preasphaltene Resin	615	150

	Relative Radical Concentration	Vanadium (ppm)
Asphaltenes	1	680
Preasphaltenes:		
Pyridine-extracted	2.8	940
THF-extracted	1.5	785
THF Insolubles	1.6	230

TABLE V. FEED AND PRODUCT COMPOSITIONS

ELEMENTAL COMPOSITION, wt%

	C	H	N	O	S	ppm Ni	ppm V	(H/C)
Coal/Resid/DCO Feed	84.47	9.55	0.52	1.68	4.35	45	177	1.36
Modified SHFT Filtrate	86.24	10.55	0.44	1.11	2.35	24	73	1.47
Modified SHFT Solids:								
Toluene Soluble	85.98	9.52	0.5	0.5	3.26	26	73	1.33
Preasphaltene	83.91	6.03	1.5	4.1	2.90	184	800	0.86
THF Soluble[1]	86.08	9.18	0.62	0.89	3.24	30	106	1.28
THF Insoluble	53.34	3.42	ND[2]	7.1	4.7	ND[2]	ND[2]	0.77

[1] Composition for this fraction determined from compositions of toluene soluble and
preasphaltene fractions weighted by the yields of these fractions, as shown in
Table II.
[2] ND = not determined

RTO/df/90339
4/23/90

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Figure 1. Schematic of Extraction Procedure

SOLIDS
(200 g)
Soxhlet Extraction
2 L Toluene

TOLUENE SOLUBLES
(TS)
Filter
0.5 uM Millipore

TOLUENE INSOLUBLES
(TI)

TRUE TS   ULTRAFINES

Soxhlet Extraction
1 L THF

THF SOLUBLES/TI
(THFS/TI)
Filter
0.5 uM Millipore

THF INSOLUBLES
(THFI)

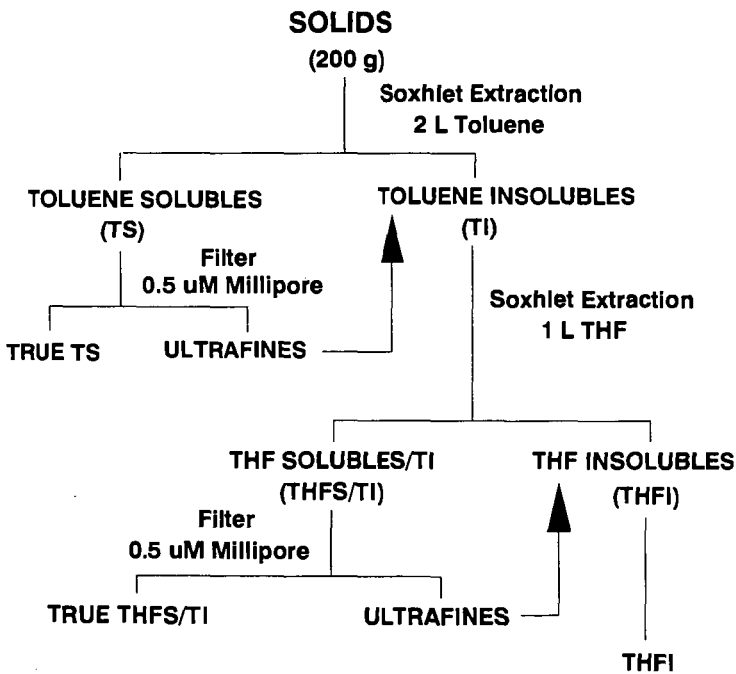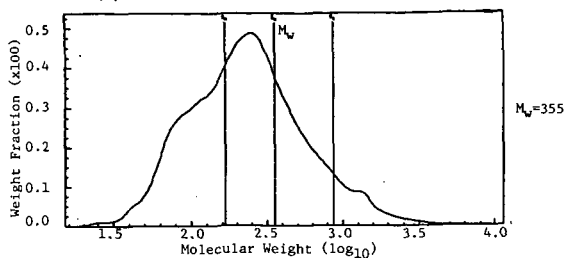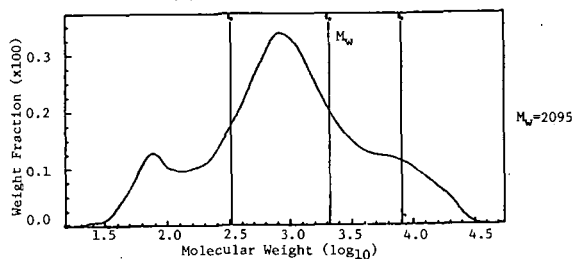TRUE THFS/TI   ULTRAFINES

THFI

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Figure 2. Molecular Weight Distributions from GPC
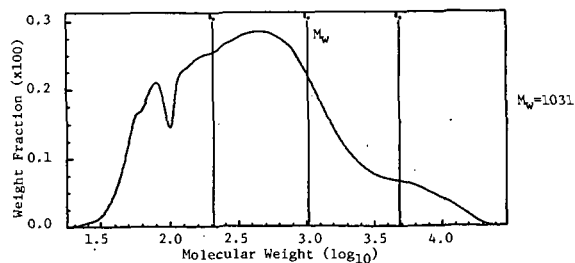### (Mw = weight-averaged molecular weight)

(a) Toluene Soluble Fraction of Coal Feed

M_w=355
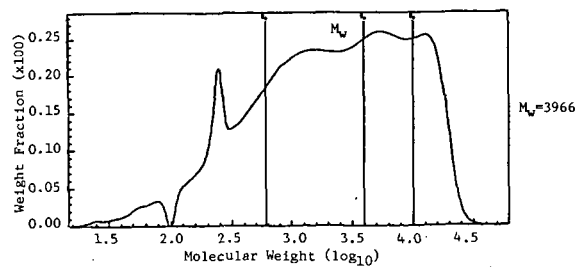
(b) 90% Resid/10% DCO Feed

M_w=2095

(c) Toluene Soluble Fraction of Coprocessing Modified SHFT Solids

M_w=1031

(d) Preasphaltene Fraction of Coprocessing Modified SHFT Solids

M_w=3966

THE SIGNIFICANCE OF HYDROGEN DONOR ABILITY AND THE CHARACTERISTICS OF HEAVY OILS/BITUMENS IN COPROCESSING

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Keywords: coprocessing; hydrogen donor ability; heavy oils/bitumens.

ABSTRACT

The hydrogen donor ability of several heavy oils/bitumens used in CANMET coprocessing and some model compounds was determined using 1,1'-binaphthyl, sulphur and a ^{13}C NMR technique. Using 1,1'-binaphthyl, it was concluded that generally heavy oils/bitumens are better hydrogen donors than model compounds such as tetralin. When sulphur was used as a hydrogen acceptor, tetralin and hydrogenated anthracene oil showed better hydrogen donor ability than any of the oils used. A good correlation was obtained between coal conversion (THF solubles, Forestburg subbituminous coal) and the per cent of transferable hydrogen determined using sulphur. In addition, the ^{13}C NMR method, which was carried out on deasphaltened heavy oils and bitumens gave slightly higher though similar values of transferable hydrogens.

The effect of "solvent" characteristics on coal and pitch conversions and distillate yields was investigated. Generally coal conversions were not affected by the type of vacuum bottoms used or solvent asphaltene content. Although the amount of indigenous saturated compounds in conventional resids was much higher than those in heavy oils/bitumens, coal dissolutions were equally effective in both types of solvents. Pitch conversions and distillate yields were shown to be more sensitive to the types of resid being processed.

Introduction

The role and importance of hydrogen donor solvents in coal liquefaction are well known and have been studied by a number of investigators (1-5). It is also known that the hydrogen donor ability of a solvent is not the only criterion that influences the degree of coal solubilization. The physical properties of the solvent also play an important role (6-7). Irrespective of whether physical and chemical properties of solvents play a significant role, the fact is that in all direct liquefaction processes the "quality" of solvent must be maintained during processing if high coal conversion and distillate yields are desired.

In coprocessing, heavy oils/bitumens which can play the role of "solvent" as in coal liquefaction, are also reactants and their roles as hydrogen donors are less understood. In general it is believed that crude derived petroleum resids and bitumens are not as good hydrogen donors compared with solvents such as tetralin, and consequently they are less effective in coal dissolution (8-9). It has been shown by Curtis et al (9) that the addition of good hydrogen donors such as tetralin and 9,10-dihydrophenanthrene in the coprocessing of Maya topped long resid and Illinois No. 6 coal promoted the production of light products.

In spite of the complexity of the chemistry involved in the recycle solvents used in direct coal liquefaction, there is no doubt that the hydrogen donor ability of the solvent is an important factor for the success of any coal liquefaction process. The question of whether the heavy oils/bitumens in coprocessing play a role as significant as that in coal liquefaction in terms of hydrogen donor ability has received little attention.

To address this question we must first understand the basic differences between the two processes. Ideally, in coprocessing there is no recycle solvent and instead fresh solvent is introduced continuously during the process. Unlike an ideal solvent in coal liquefaction, this coprocessing "solvent" is also a reactant and it is upgraded simultaneously with the coal and its chemical composition changes significantly during processing. In CANMET

coprocessing, a mixture of coal and heavy oils/bitumen is processed in a single-stage once-through operation using iron sulphate as a disposable catalyst. Previous results from our laboratory (10) indicated that the *dissolution* of low-rank Canadian coals was relatively insensitive to the type of bitumen or petroleum resid used. However, *resid conversion* depended on the type of resid employed.

The objectives of the present work were: 1) to determine quantitatively the hydrogen donor abilities of different heavy oils/bitumens and conventional crude derived petroleum resids used as oil feedstocks in CANMET coprocessing and attempt to correlate coal dissolution to the amount of transferable hydrogens available in each and 2) to investigate the effect of "solvent" characteristics on coal and pitch conversions.

Experimental

Materials and Feedstocks

Three crude derived petroleum resids, Boscan, Blend 24 (Venezuela), Maya (Mexico) and Athabasca bitumen and Lloydminster heavy oil vacuum bottoms were obtained from the sample bank of the Primary Upgrading Section, Energy Research Laboratories. IPPL (a vacuum resid from a mixture of sweet crudes from Western Canada) was supplied by the Esso Refinery, Sarnia, Ontario. Cold Lake vacuum bottoms (CLVB) was obtained from the Strathcona refinery of Imperial Oil Ltd, Alberta. Forestburg subbituminous coal from Alberta was supplied by Luscar Limited. Its analysis is shown in Table 1. The 1,1'-binaphthyl from Aldrich was used as received. Raw anthracene oil and hydrogenated anthracene oil were obtained from the Nova Scotia Research Foundation Corporation. The characteristics of the solvents and oils used in this work are shown in Tables 2 and 3.

H-donor measurements using 1,1'-Binaphthyl

For these experiments, the procedure of Kline et al was used (11). The 2-mL reaction vessels were made from 316 SS tubing with end caps. Each sample (0.5 g) was placed in the vessel with 0.5 g 1-1'-binaphthyl and 1.5 g benzene as solvent. The vessels were weighed before the experiment and heated to 430°C for 1 h. A Tecam model IFB 101 fluidized bed sand bath was used as the heating medium. About 2-3 min were required for the reaction vessels to reach the reaction temperature. The vessels were quenched in water, then dried and weighed. Experimental runs having greater than 100 ± 5 wt % material balance were discarded. Each experiment was carried out at least in duplicate.

The contents of the vessels were extracted using THF and analyzed by gas chromatography using a Perkin Elmer Sigma 2000 equipped with 15 m SE-54 capillary column and 3600 data station. The analyses were performed with split mode using an internal standard method. The product analyses were carried out at an initial column temperature of 200°C for 5 min, then temperature programmed at 5°C/minute to 300°C.

H-donor measurements using sulphur

The method used by Aiura et al. for determining transferable hydrogen in coal-derived solvents was modified (H_2S was quantified by a gas chromatography method rather than by titration) and applied for measuring the donatable hydrogen in bitumens/heavy oils (12). Dehydrogenation experiments using sulphur were performed in a 100 mL stainless steel microreactor at 235±3°C and 1 h residence time. The reactor was charged with 5 g solvent to be tested for donatable hydrogen, 4 g sulphur as hydrogen acceptor and 15 g of phenanthrene as diluent. The reactor was shaken vertically and to aid mixing, two stainless steel balls were placed in the reactor which was pressurized to 100 psig with N_2 at room temperature. After the required residence time the reactor was cooled to room temperature and the gases (H_2S and N_2) were collected in a gas bag. The total volume of the gas was measured by water displacement and the composition was determined using a Perkin Elmer Sigma-1B gas chromatograph. From the amount of H_2S formed, the transferable hydrogen was then determined.

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Compound type separation and H-donor measurements using ^{13}C NMR

The amount of transferable hydrogen in four heavy oils/bitumens and conventional resids was also measured using ^{13}C NMR according to the method described by Aiura et al. (12). The measurements were carried out on the pentane soluble fractions of the materials (asphaltene free). The pentane soluble fractions were separated on a silica column using a Waters 500 preparative chromatograph into saturates (pentane eluted), aromatics (toluene eluted) and polars (methylene chloride and back flash with methyl-tert-butyl ether eluted). The saturated fractions and the original samples (asphaltene free) were subsequently analyzed by ^{13}C NMR using a Varian XL 300. The amount of transferable hydrogen was calculated from the integrated intensities in the 21-37 ppm range, the carbon contents of the original and the saturated fractions, and the weight per cent of the saturated fractions.

Coprocessing experiments

The coprocessing experiments were carried out in 100 mL stainless steel batch autoclaves equipped with thermowells and pressure transducers. Approximately 20 g of feedstock was placed in the reactor then pressurized with either H_2 or N_2 to 800 psig at room temperature. Using a sand bath, about 3 min were required for the reactor to reach the reaction temperature of 420°C. At the end of a run, the reactor was quenched in a water bath. The reactions were carried out either in the presence or absence of iron sulphate catalyst. The iron concentration was kept constant at 0.6 wt % based on maf slurry charged. The volume of the gaseous products was measured and their compositions were analyzed by a gas chromatograph. The slurry products were extracted using pentane, toluene and THF to determine the amount of oils, asphaltenes, and preasphaltenes respectively. Coal conversions were determined from the amount of THF insolubles. Pitch conversions data shown in Table 6 were obtained using a continuous bench scale coprocessing unit.

Results and Discussion

Using 1,1'-binaphthyl as H-acceptor

The relative hydrogen donor abilities of heavy oils/bitumens and some model compounds measured using 1,1'- binaphthyl are shown in Table 4. At 430°C and in the presence of the hydrogen donors listed in Table 4, 1,1'- binaphthyl is converted to perylene (P) as a major product. Small amounts of rearranged product 2,2'-binaphthyl and a negligible amount of 1,2-binaphthyl were also obtained. The mole ratios of perylene (P) to the sum of 1,1'-binaphthyl plus its rearranged product 2,2'-binaphthyl (B) were taken as measures of the strength of hydrogen donation. The P/B ratios listed in Table 4 are corrected for the amount of perylene formed by heating 1,1'-binaphthyl in the absence of hydrogen donors.

The hydrogen donor abilities for tetralin and 9,10-dihydroanthracene in Table 4 are consistent with those reported by Kline et al (11). The higher values of P/B reported by Kline et al, are attributed to the higher temperature (470°C) employed. For bitumens/heavy oils the P/B ratios remained relatively constant. According to these results using 1,1'-binaphthyl as a hydrogen acceptor, the heavy oils/bitumens tested are better hydrogen donors than tetralin. The mechanism of hydrogen transfer from donor solvents to 1,1'-binaphthyl to form perylene is not well known. It is also unclear why tetralin, which is a good hydrogen donor, does not interact with this reagent as well as heavy oils/bitumens to form perylene. There may be other factors such as physical interactions (favouring heavy oils) that influence the reaction path leading to perylene formation.

In order to correlate the hydrogen donor abilities of bitumens/heavy oils (P/B) for different solvents with coal conversions the dissolution of Forestburg subbituminous coal was studied. In these experiments coal is used as a hydrogen acceptor. Since the objective was to determine the degree of hydrogen transfer from the solvents only to the coal, the experiments were carried out in a nitrogen atmosphere. To prevent coke formation, coal

solubilizations were carried out at a short reaction time of 5 min. The coal conversion results at 5 min in the nitrogen atmosphere and those from 30 min in a-hydrogen atmosphere are also shown in Table 4. For comparison, the results of the liquefaction of the same coal in tetralin under similar conditions are given. For the heavy oils/bitumens, coal conversion into THF solubles remained relatively constant. In the nitrogen atmosphere there is a substantial difference in coal conversion between tetralin and the bitumens/heavy oils. In the hydrogen atmosphere the differences are much smaller. As shown in Table 4 it can be concluded that using 1,1'-binaphthyl as a hydrogen acceptor no general correlation can be obtained between P/B and coal conversions for heavy oils/bitumens and model compounds.

Using sulphur as H-acceptor

Hydrogen donor abilities obtained for heavy oils/bitumens, tetralin, hydrogenated anthracene (HAO) and raw anthracene oils (RAO) using sulphur are shown in Table 5. The amount of transferable hydrogen (TH) for each material was calculated from the amount of H_2S formed in the reaction of sulphur with these materials. Tetralin and HAO showed the highest amount of TH whereas RAO showed the lowest amount of TH. For the heavy oils/bitumens the weight per cent of TH did not change significantly and remained constant at about 1 wt %.

The coal conversion data both in H_2 (30 min) and N_2 (5 min) atmospheres are also shown in Table 5. Using sulphur as a hydrogen acceptor appears to give a better general correlation between coal conversions and hydrogen donor abilities. The exception to this is between HAO and tetralin where coal conversion (in N_2) is significantly higher in HAO (lower TH) than in tetralin.

The results indicate that other factors besides hydrogen donor abilities influence coal dissolution. In a hydrogen atmosphere aromatic hydrocarbons present in the solvents with deficient donatable hydrogens become hydrogen shuttlers transferring hydrogen from the gas phase to the free radicals from coal. Since significant amounts of different aromatic structures are present in the heavy oils/bitumens listed in Table 5, relatively high coal conversions are obtained in a hydrogen atmosphere and the difference in coal conversions between any one of these solvents and a relatively good hydrogen donor such as HAO becomes small.

The results also show that although the amount of transferable hydrogen in RAO is considerably lower than the heavy oils/bitumens listed in Table 5, the coal conversion (in N_2) is similar or higher in this solvent. It can be argued that sulphur may indiscriminately abstract hydrogen from different positions within the molecules of heavy oils/bitumens and that the TH values reported in Table 5 for these materials are not true values for the available hydrogen in hydroaromatic positions. However, as discussed below there is good agreement between dehydrogenation using sulphur and the ^{13}C NMR methods. Again, other properties of the solvents (like physical properties) may play an important role in coal dissolution besides hydrogen donor ability.

The amount of transferable hydrogen of four heavy oils/bitumens as determined by ^{13}C NMR is also shown in Table 5. The weight per cent of TH was obtained using the deasphaltened fraction of these materials. The ^{13}C NMR TH values are comparable (within 0.3 for Blend 24 and Athabasca) with the sulphur dehydrogenation method. Irrespective of the method of TH determination, it appears that heavy oils/bitumens having the same amount of TH are capable of dissolving coal to the same degree.

Effect of heavy oil/bitumen characteristics on coal and pitch conversions

Lett et al (8) in their investigation of the hydrogen donor abilities of heavy oils concluded that heavy oils containing more asphaltenes are better hydrogen donors than those with less asphaltenes. The data presented in Table 5 show that this claim cannot be generalized. Although Athabasca bitumen contains much higher asphaltenes than Blend 24 (Table 3) the amount of transferable hydrogen (measured by ^{13}C and sulphur dehydrogenation methods) and coal conversions is similar. It has also been pointed out by

Curtis et al (13) that the presence of saturated compounds in liquefaction solvents results in lower coal conversions. The data obtained in our laboratory have shown that in coprocessing, the dissolution of coal is not significantly affected by the amount of saturated compounds present in heavy oils/bitumens. Table 6 shows the compositional characteristics of four heavy oils/bitumens. Although the amount of the saturated fraction is more than twice in Maya compared with Athabasca, the coal conversion did not change significantly (Table 6). However, as was shown earlier by Fouda and Kelly (10), distillate production in coprocessing is sensitive to the type of resid processed. In general, under coprocessing conditions, conventional resids containing higher saturated fractions than bitumens usually produce lower distillate yields and pitch conversions.

Conclusions

The degree of hydrogen donor ability of heavy oils/bitumens as determined by three different methods was shown to be very similar at least for the heavy oils/bitumens tested. These coprocessing solvents contain approximately 1 wt % transferable hydrogens and are capable of dissolving about 86 wt % coal in a hydrogen atmosphere and about 20 wt % in a nitrogen atmosphere irrespective of their origin. A relatively good correlation was obtained between coal conversion and transferable hydrogens using sulphur as a hydrogen acceptor. The data presented in this paper also show that the weight per cent of saturated fraction and asphaltenes in the heavy oils/bitumens (under CANMET coprocessing conditions) does not influence the degree of coal conversion. It can also be concluded that the hydrogen donor ability of heavy oil/bitumen is not a determining factor in coal solubilization in catalytic coprocessing and definitely is not as significant as in direct coal liquefaction. It is suggested that under a hydrogen atmosphere the aromatic hydrocarbons can act as hydrogen shuttlers transferring hydrogen from the gas phase to coal derived radicals.

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Table 1 - Analysis of Forestburg coal

Proximate analysis
(wt %, as received)

Moisture	14.09
Volatile matter	36.37
Fixed carbon	42.67
Ash	6.87

Ultimate analysis
(wt % daf)

C	71.99
H	4.64
N	1.78
O	20.98
S	0.61

Table 2 - Elemental Analyses of Oil Feedstocks (wt %)

Solvents/Oils	C	H	N	O	S
CLVB[a]	82.82	10.57	0.78	0.35	5.66
CLVB(P)[b]	82.62	10.27	0.83	0.26	5.79
Boscan	80.96	10.24	0.90	0.24	5.73
Boscan(P)[b]	81.97	9.83	1.09	0.29	6.40
Maya	84.80	10.10	0.42	< 0.50	4.30
Blend 24[c]	84.31	10.90	0.81	0.33	3.45
Athabasca	82.30	9.60	0.67	0.69	5.96
IPPL[d]	86.40	10.90	0.43	< 0.50	1.71
Lloydminster	83.20	9.84	0.54	0.61	5.73
Raw anthracene oil	91.50	5.74	1.04	0.56	0.58
Hydrogenated anthracene oil	90.60	9.10	0.15	0.26	0.00

[a] Cold Lake vacuum bottoms, [b] +525°C fractions, [c] Venezuela blend vacuum bottoms,
[d] vacuum bottoms from a blend of Western Canadian crudes (IBP = 560°C)

Table 3 – Characteristics of Heavy Oil/Bitumen Feedstocks

Solvents/ Oils	Pentane Inso.(wt %)	Toluene Inso.(wt %)	Pitch[a] wt %	CCR wt %	gravity (°API)	Mn[1]	fa[2]
CLVB[b]	23.5	0.20	83.2	17.1	4.82	788	31
Boscan	22.3	0.09	64.6	16.7	7.77	613	30
Maya	22.3	0.11	86.0	18.4	----	756	34
Blend 24[c]	21.5	<0.10	95.1	18.6	6.95	848	30
Athabasca	38.4	1.21	99.3	23.9	1.49	983	34
IPPL[d]	14.0	0.92	100.0	15.6	9.86	910	30
Lloydminster	37.4	0.22	90.7	22.0	3.39	1081	35

a +525°C fraction, b cold Lake vacuum bottoms, c Venezuela blend vacuum bottoms,
d vacuum bottoms from a blend of Western Canadian crudes (IBP=560°C),
1 number average molecular weight (VPO),
2 aromaticity (^{13}C NMR)

Table 4 – Hydrogen donor abilities of model compounds and heavy oils/bitumens measured using 1,1'-binaphthyl and conversion of Forestburg coal

Material	P/B x 100[a]	Coal conversion[b] H_2	Coal conversion[c] N_2
1,1'-Binaphthyl	0.19	---	---
Tetralin	0.51 (1.3)[4]	91.7	59.8
9,10-Dihydroanthracene	10.00 (17.7)[4]	---	---
CLVB[1]	5.50	88.7	22.1
CLVB(P)[2]	6.90	---	---
Boscan	5.40	88.3	20.1
Boscan(P)[2]	7.20	85.1	21.3
Maya	7.00	82.7	19.1
Blend 24[3]	5.70	86.7	21.9

a moles of perylene to moles of 1,1'-binaphthyl + moles of byproducts
b conversion to THF solubles at 420°C, 30 min and 800 psi H_2
c conversion to THF solubles at 420°C, 5 min and 800 psi N_2
1 Cold Lake vacuum bottoms, 2 +525°C fractions, 3 Venezuela blend vacuum bottoms
4 values taken from reference 11.

Table 5 - Comparison of hydrogen donor abilities of different solvents/oils and coal conversions.

Solvents	Transferable hydrogen (wt %)		Coal conversion (wt %, maf)	
	Sulphur	^{13}C NMR	H_2, 30 min.	N_2, 5 min
Tetralin	2.01	---	91.7	59.8
CLVB[a]	1.20	1.28	88.7	22.1
Blend 24[b]	1.01	1.32	86.5	21.9
Athabasca	1.02	1.30	86.6	20.8
Maya	1.07	1.13	82.7	19.1
Boscan	1.24	---	88.3	20.1
Boscan (P)[c]	1.17	---	85.1	21.3
IPPL[d]	0.98	---	83.7	19.1
Lloydminster	1.18	---	86.6	20.0
Raw anthracene oil	0.33	---	72.1	26.1
Hydrogenated anthracene oil	1.82	---	94.8	78.2

[a] Cold Lake vacuum bottoms, [b] Venezuela blend vacuum bottoms [c] +525°C fractions, [d] vacuum bottoms from a blend of Western Canadian crudes (IBP=560°C)

Table 6 - Hydrocarbon type separation of heavy oils/bitumens (wt %): Effect of solvent Characteristics on coal and pitch conversions.

Solvent/Oils	Saturates	Aromatics	Polars	Coal conv.	Pitch conv.[c]
CLVB[a]	28.66	58.68	12.66	88.7	34.1 (68.4)
Athabasca	19.50	65.81	14.68	86.6	40.6 (69.0)
Blend 24[b]	36.38	51.13	12.49	86.5	36.0 (62.2)
Maya	41.51	50.82	7.68	82.7	---- (----)

[a] Cold Lake vacuum bottoms, [b] Venezuela blend vacuum bottoms, [c] results from continuous operation at 425°C and (450°C)

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THE CATALYTIC ACTIVITY OF ORGANOMETALLIC COMPLEXES IN COPROCESSING

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Keywords: coprocessing, organometallic complexes, coal liquefaction

ABSTRACT

The catalytic activity of molybdenum, nickel, and vanadium, generated *in situ* from their organometallic complexes, as well as a presulfided powdered $NiMo/Al_2O_3$ was evaluated in coal-oil coprocessing. The coprocessing reactions were conducted both thermally and catalytically with Illinois No. 6 coal and Khafji or Maya residuum. The activities of molybdenum, nickel, and vanadium present as metal sulfides for converting coal and upgrading petroleum residuum were compared, and the possibility of indigenous nickel and vanadium catalysis in coprocessing was explored.

INTRODUCTION

The coprocessing of coal with petroleum residuum simultaneously upgrades coal, coal liquids and residuum into higher quality products[1-3]. When compared to coal liquefaction, coprocessing is attractive for several reasons[4]. Coprocessing uses a sufficient amount of low-cost petroleum residuum as the processing solvent without the extensive requirement of solvent recycling so that it produces larger volumes of hydrocarbon liquids than does the liquefaction of coal alone. Because coal is partially soluble in asphalt and residuum, less severe reaction conditions are required in coprocessing than in coal liquefaction. Therefore, coke formation is also reduced. In addition, coprocessing can utilize the existing upgrading facilities used for petroleum refining.

Catalytic coprocessing is more desirable than thermal coprocessing[5]. The role of the catalyst in coprocessing is substantial. The amount of coal conversion, the extent of heteroatom removal and saturation of aromatic compounds, and the product distribution in terms of the solubility of fractions, such as oil, asphaltenes, preasphaltenes and insoluble organic matter (IOM), in catalytic coprocessing is influenced by the catalyst used. This experiment evaluated and compared the effects of catalytically active species of Mo, Ni and V generated *in situ* from their organometallic complexes in a sulfur-rich environment on the upgrading of coal and petroleum residuum in coal-oil coprocessing.

Upgrading of coal and petroleum residuum may be achieved by several types of hydrogenation reactions: hydrogenolysis of carbon-carbon bonds or carbon-heteroatom bonds, producing smaller molecular structures, hydrogenation of compounds containing aromatic rings, producing more saturated hydrocyclic compounds, and removal of heteroatoms (S, N, O), producing more environmentally acceptable products with lower sulfur, nitrogen and oxygen contents. From past experience in hydrogenation reactions with model compounds[6,7], each

metal species is expected to show different catalytic activity and selectivity for various types of hydrogenation reactions occurring in coal-oil coprocessing. In this experiment, the catalytic activity and selectivity of different metals in upgrading actual coal and residuum in coprocessing reactions are compared. These experimental results are expected to be useful in evaluating the degree to which the catalytic character of each metal species is attributable to specific types of hydrogenation reactions in coprocessing. The possible catalytic activity of Ni and V indigenous to the residuum used as the solvent in coprocessing is also discussed.

EXPERIMENTAL

Feed Materials. Khafji and Maya petroleum residua and Illinois No.6 coal were selected as feed materials for coprocessing reactions. All of these materials were supplied by Amoco Oil Company. Khafji and Maya were used as received, but Illinois No. 6 coal was pulverized to 100 mesh and kept in a vacuum desiccator before use. The moisture content (6.3 wt%) and ash content (9.8 wt%) of Illinois No. 6 coal were obtained by Auburn University and used in the calculation of experimental results.

Catalyst. Organometallic complexes of transition metals, such as Mo, Ni and V, as well as a supported bimetallic NiMo/Al$_2$O$_3$, were used as coprocessing catalysts. The precursors of the active metal species of Mo, Ni and V were obtained in the form of an oil-phase naphthenate or octoate, or a solid-phase acetylacetonate and were supplied by Air Products, Shepherd Chemical, Strem Chemical, and Aldrich. The metal contents in the precursors supplied were 3 to 23 wt%. Each catalyst precursor was diluted by n-hexadecane to enhance its fluidity and to keep the metal content consistent in the precursor at 3 wt% of Mo or Ni and 1.5 wt% of V. A solid catalyst, Shell 324 NiMo/Al$_2$O$_3$, was presulfided in a heated gas stream of 10 vol% H$_2$S in H$_2$ and then pulverized to 150 mesh before use.

Thermal and Catalytic Reactions. The coprocessing reactions were performed in 56 cm^3 tubing bomb microreactors which were made of 316 stainless steel and horizontally oriented during reactions. Each coprocessing reaction was conducted with 3g of coal and 6g of Khafji or Maya residuum under reaction conditions of 1250 psig H$_2$ charged at ambient temperature (about 2820 psig at 400°C and 3000 psig at 425°C), 400°C or 425°C reaction temperature, one hour reaction time, and 550 cpm vertical shaking. In catalytic reactions, each catalyst paste or solid catalyst was introduced at the level of approximately 3000 ppm metal in the feed. In cases of organometallic complexes being used as catalyst precursors, elemental sulfur was added in an amount sufficient to produce metal sulfide *in situ* from each organometallic precursor; 0.038g for thermal reaction, 0.057g for Mo, 0.032g for Ni, and 0.077g for V.

Analysis. The coprocessing products from 3g coal and 6g residuum were fractionated by three different solvents: first, the oil fraction was extracted by hexane; next, the asphaltene fraction was extracted by toluene; finally, the preasphaltene fraction was extracted by tetrahydrofuran. About 9g of the whole product recovered from the coprocessing reaction was dissolved in a total of 450 ml hexane: the recovered product was dissolved in 150 ml hexane, sonicated for 4 minutes, centrifuged to separate hexane solubles and hexane from undissolved product materials, and then all of these procedures were repeated twice. Next, the hexane insolubles were dissolved in 450 ml toluene, and then the toluene insolubles separated from the extraction with toluene were dissolved in 450 ml tetrahydrofuran and extracted using similar procedures as with hexane. The amount of each fraction was compared in terms of gas, oil (hexane soluble), asphaltenes (hexane insoluble but toluene soluble), preasphaltenes

(toluene insoluble but tetrahydrofuran soluble), and insoluble organic matter (IOM - tetrahydrofuran insoluble) on a moisture, ash and catalyst free basis. The amount of gas product produced from the reaction was determined by H_2 analysis using a Varian 3700 gas chromatograph with a 15 m stainless steel column (1/8 inch OD) packed with mixed molecular sieve 13A (75 wt%) and molecular sieve 5A (25 wt%) and with a thermal conductivity detector. Reactions were usually duplicated, and the product distribution and the coal conversion were expressed as the average values. A statement of error is given in the tables.

RESULTS AND DISCUSSION

<u>Efficacy of Coprocessing.</u> The efficacy of coprocessing was evaluated by testing the effect of petroleum residuum on the extent of coal hydrogenation. Three grams of Illinois No. 6 coal were hydrogenated, both thermally and catalytically with Mo naphthenate, with 6g of different solvents: n-hexadecane, which appeared to be nearly nonreactive at the reaction conditions and was soluble in hexane, and Khafji and Maya residua, which were more reactive processing solvents. Each fraction produced from Illinois No. 6 coal was determined by subtracting the amount of that fraction produced from the hydrogenation reaction of 6g of Khafji or Maya alone at equivalent reaction conditions from the overall amount of the same fraction produced from the coprocessing reaction. Khafji and Maya produced more hexane and toluene solubles (oil and asphaltenes) than did n-hexadecane in both thermal and catalytic reactions. In the thermal reactions, the amount of oil and asphaltenes produced from Illinois No. 6 coal was about 7 wt% with n-hexadecane, 24 wt% with Khafji, and 13 wt% with Maya. In the catalytic reactions with Mo naphthenate, the amount of the same fractions produced from Illinois No. 6 coal was about 32 wt% with n-hexadecane, 56 wt% with Khafji, and 53 wt% with Maya. This result indicated that the petroleum residuum enhanced hydrogenation of heavy fractions produced from coal such as preasphaltenes to lighter fractions such as oil and asphaltenes or enhanced the dissolution of the fractions produced from coal in the extracting solvents.

<u>Catalytic Activity of *In Situ* Generated Metal Species in Coprocessing.</u> The activities of Mo, Ni, and V catalysts generated *in situ* from their organometallic complexes in coprocessing were evaluated and compared to each other and that of a presulfided powdered NiMo/Al$_2$O$_3$ catalyst at equivalent reaction conditions. The organometallic precursors of each metal were in the form of naphthenate, octoate, or acetylacetonate as shown in Table 1. The total active metal loading for each catalyst was about 3000 ppm of the feed materials. Even though sulfur was released from the feed materials during the reaction, a sufficient amount of elemental sulfur was added to generate metal sulfide from each precursor from the beginning of the reaction[8,9]. In the coal-Khafji coprocessing reactions, the Mo and Ni species were the most active for producing toluene solubles (oil and asphaltenes) and for converting coal. The different V species regardless of precursor structure used were the least active (Table 1).

As the reaction temperature was raised from 400°C to 425°C, the recovery of the products decreased from 97 - 100% at 400°C to 85 - 95% at 425°C. This decreased recovery most probably resulted from coking of the coal and residuum materials at the higher reaction temperature in both the thermal and catalytic reactions. In addition, gas production increased from 1 - 2.5 wt% at 400°C to 4 - 5.5 wt% at 425°C. Thermal reaction and catalytic reactions with Mo naphthenate and NiMo/Al$_2$O$_3$ converted more coal at higher temperature, but reactions with the other catalysts, especially vanadylacetylacetonate, showed reduced coal conversion at 425°C. In thermal and catalytic coprocessing reactions, the actual amount of oil

and asphaltenes produced from coal at 425°C was nearly similar to or sometimes less than that at 400°C. Only Mo naphthenate appreciably enhanced the production of toluene solubles at higher temperature. These results indicated that a high reaction temperature frequently induced the production of more gaseous products and coke as well as other retrogressive reactions producing additional heavier fractions like preasphaltenes and IOM.

The high activity of Mo and Ni species and the low activity of V species were again confirmed in coal-Maya coprocessing reactions (Table 1). The hydrogen consumption in each reaction generally followed the activity of the catalyst used; more hydrogen consumption was observed with Mo, Ni, and NiMo/Al_2O_3 catalysts than with V catalysts or no catalyst.

Effect of Sulfur. Even though sulfur species, such as H_2S, were produced from feed materials during the reaction, elemental sulfur was usually added to the catalytic reactions to promote the production of metal sulfides *in situ* from the organometallic complexes. The effect of additional sulfur on the activity of the different catalysts, such as sulfur-sensitive Ni species[7] and sulfur insensitive Mo and V species, was evaluated in coal-Khafji coprocessing (Table 2). Elemental sulfur was added in an amount three times the quantity of sulfur required to produce a metal sulfide from each metal (MoS_2, Ni_3S_2 and V_2S_3). At both reaction temperatures, 400°C and 425°C, additional sulfur usually enhanced the production of oil and asphaltenes and the conversion of coal in both thermal and catalytic reactions except for the reactions with Ni octoate. The reason for the lowered activity of Ni octoate by sulfur has not yet been clearly explained. However, the activity of sulfur-sensitive Ni catalysts in coprocessing was not much affected by additional sulfur: the Ni species was still effective in converting coal and producing fractions of oil and asphaltenes.

Infrared Analysis of Coprocessing Products. Illinois No. 6 coal, residua, and various fractions extracted from coprocessing reactions have been analyzed qualitatively and quantitatively by conventional Fourier transform infrared (FTIR) spectrometry. The relationship between the catalytic activity observed and the infrared spectrum has been examined. The infrared spectrum of the oil fraction from the coprocessing reaction was very similar to that of the residuum used, predominantly showing aliphatic character with only a slight amount of aromatic character. However, the infrared spectrum of asphaltenes from the coprocessing reaction showed more coal character than oil, showing increased aromatic C-H stretch at 3050 cm^{-1}, aromatic ring stretch at 1585 cm^{-1}, and aromatic C-H out-of-plane bending at 860, 815, and 750 cm^{-1}. The infrared spectrum of preasphaltenes was the most similar to that of the coal used; the peaks indicating increased aromatic character and some other peaks indicating C-O stretch, C-C stretch, and O-H bending between 950 and 1300 cm^{-1}, that were not found in the spectrum of oil fraction, resembled the peaks in the spectrum of coal. The relationship between the activity of different catalysts and the infrared spectrum of the product obtained with each catalyst used is under study.

CONCLUSIONS

The activity of *in situ* generated molybdenum, nickel and vanadium catalysts as well as the effect of sulfur on them in upgrading coal and petroleum residuum was evaluated. Petroleum residua enhanced production of toluene solubles from coal compared to the nonreactive solvent, n-hexadecane. Catalytic coprocessing reactions usually produced more oil and asphaltenes than did thermal coprocessing.

In the thermal coprocessing reactions, elemental sulfur introduced at a level of 0.004 g per gram of the mixed reactant of coal and residuum slightly enhanced the extent of oil production and produced less IOM fraction than the thermal reactions without additional sulfur. In the catalytic coprocessing reactions, *in situ* generated Mo and Ni species showed high levels of oil production and coal conversion. But *in situ* generated V species showed low activity similar to that of the additional sulfur in thermal reactions or even lower than the thermal reactions without sulfur depending on organic precursors of V used. A higher reaction temperature of 425°C did not activate V species as much as it did Mo and Ni species. The activities of *in situ* generated metal species (possibly metal sulfides) and a commercial presulfided $NiMo/Al_2O_3$ at the same metal loading of 3000 ppm for converting coal and simultaneously upgrading coal and residuum were observed in the following order.

Mo species ≈ Ni species > $NiMo/Al_2O_3$ > Thermal with sulfur ≥ V species.

Additional sulfur usually enhanced the activity of catalysts in coprocessing except for Ni species from Ni octoate. However, even in the presence of sulfur, the Ni species still showed high activity for coal conversion and oil and asphaltene production. These results indicated that indigenous nickel can be a possible coprocessing catalyst if its precursors in the feed materials are properly concentrated. V, which is usually more abundant in petroleum residuum than is Ni, appeared to have minor catalytic activity for converting coal and residuum to lighter fractions. However, the V sulfide species *in situ* generated showed high activity for heteroatom removal and partially saturating aromatic structures of model chemicals[10]. To understand this discrepancy between the activity of V sulfide species in model and actual coprocessing reactions, a study on the stoichiometry of active V sulfides *in situ* generated in both model and actual coprocessing reactions is required.

ACKNOWLEDGEMENTS

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Table 1. Coprocessing Reactions of Illinois No. 6 Coal and Khafji or Maya Residuum[1]

Reaction Conditions and Catalysts[2]	Product Distribution (wt%)[3]			Toluene Solubles[4]	Coal Conversion(%)
	Oil	Asp	Preasp		
Khafji					
No Reaction	57.5	13.3	2.0	70.8	NA[5]
400°C Reaction					
Thermal Reaction	56.1	17.5	11.4	73.6	56.3 ±2.0[6]
VO Acetylacetonate	55.1	17.9	11.3	73.0	53.2 ±3.4
NiMo/Alumina	58.3	17.4	10.2	75.7	61.9 ±0.6
Ni Acetylacetonate	59.1	18.9	16.6	78.0	86.9 ±2.5
Ni Octoate	61.6	18.4	11.6	80.0	78.0 ±0.4
Mo Naphthenate	61.8	22.3	9.6	84.1	86.4 ±6.7
425°C Reaction					
Thermal Reaction	50.8	17.0	13.4	67.8	60.0
VO Acetylacetonate	48.1	14.0	16.5	62.1	44.6
V Acetylactonate	53.5	17.5	13.6	71.0	69.2
V Naphthenate	55.2	16.9	13.0	72.1	65.0
NiMo/Alumina	60.5	16.0	7.5	76.5	68.5
Ni Octoate	60.2	16.8	9.8	77.0	72.4
Ni Acetylacetonate	60.5	18.7	11.4	79.2	84.8
Ni Naphthenate	62.5	17.3	6.4	79.8	72.4
Mo Octoate	66.7	17.0	3.6	83.7	77.0
Mo Naphthenate	70.3	20.4	3.3	90.5	95.0
Maya					
No Reaction	46.4	23.7	1.6	70.1	NA[5]
400°C Reaction					
Thermal Reaction	49.9	18.7	9.9	68.6	37.4 ±0.2[6]
V Naphthenate	45.6	21.5	13.4	67.1	50.7 ±1.4
Ni Naphthenate	51.1	23.1	17.8	74.2	82.8 ±4.1
NiMo/Alumina	52.2	24.3	11.0	76.5	67.7 ±3.5
Mo Naphthenate	56.7	23.7	7.0	80.4	66.9 ±0.1

[1] Overall product distribution based on the fractions produced from both coal and residuum was compared. The reactions performed at 400°C were duplicated and sometimes repeated more than twice, and the results were expressed as the average values. The standard deviation ($\pm \sigma_n$) of each fraction varied in the range of zero to 1.9 wt% (usually zero to 0.7 wt%) with Khafji residuum and in the range of 0.1 to 3.2 wt% (usually 0.1 to 0.9 wt%) with Maya residuum. The reactions performed at 425°C were conducted once.

[2] Abbreviations: V(vanadium), VO(vanadyl), Ni(nickel), and Mo(molybdenum). Additional sulfur: 0.037g for thermal reaction, 0.080g for V and VO, 0.031g for Ni, and 0.058g for Mo.

[3] The products were fractionated into gas, oil, asphaltenes(Asp), preasphaltenes(Preasp), and IOM.

[4] Toluene solubles (oil and asphaltenes)

[5] NA: Not available

[6] Standard deviation ($\pm \sigma_n$) of coal conversion (%)

Table 2. Effect of Sulfur on Coal-Khafji Coprocessing[1]

Coprocessing at 400°C \	Thermal	VOAcAc	NiAcAc	NiOct	MoNaph
Without Sulfur					
Oil (wt%)	52.8±1.6	54.4±1.1	58.3±0.1	60.0±0.1	60.0±0.2
Asphaltenes (wt%)	17.2±0.3	17.4±1.5	19.0±0.3	18.1±0.9	20.0±0.4
Coal Conversion (%)	46.9±1.6	42.7±2.8	85.3±1.7	78.7±2.5	76.3±1.3
With Sulfur[2]					
Oil (wt%)	56.1±0.7	55.1±1.0	59.1±0.7	61.6±0.3	61.8±1.2
Asphaltenes (wt%)	17.5±0.2	17.9±1.2	18.9±0.0	18.4±0.0	22.3±1.9
Coal Conversion (%)	56.3±2.0	53.2±3.4	86.9±2.5	78.0±0.4	86.4±6.7

Coprocessing at 425°C \	Thermal	VOAcAc	NiAcAc	NiOct	MoOct	MoNaph
Without Sulfur						
Oil (wt%)	52.5	51.9	55.5	65.6	68.3	69.9
Asphaltenes (wt%)	14.0	12.9	17.7	16.6	15.3	18.0
Coal Conversion (%)	50.3	40.5	80.4	77.1	76.4	92.2
With Sulfur[2]						
Oil (wt%)	55.6	50.8	62.6	62.0	71.2	73.2
Asphaltenes (wt%)	15.4	13.2	17.8	16.0	14.7	18.4
Coal Conversion (%)	60.0	44.6	84.8	72.4	77.0	95.0

[1] The product distribution was expressed as the average values and standard deviations ($X \pm \sigma_n$) based on the fractions of overall products from both coal and residuum in coprocessing. The reactions performed at 400°C were duplicated and sometimes repeated more than twice, and the reactions at 425°C were performed once.
   Abbreviations: VOAcAc (vanadium actylacetonate), NiAcAc (nickel acetylacetonate), NiOct (nickel octoate), MoOct (molybdenum octoate), and MoNaph (molybdenum naphthenate).
[2] Additional sulfur amount: 0.038g for thermal reactions, 0.080g for V, 0.031g for Ni, and 0.058g for Mo species.

NATURAL COPROCESSING OF COAL AND TAR

by

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ABSTRACT

This study examines optically the interaction between coal and coal-tar pitch in a self-burning coal setting. Three distinct zones, a thick, lower carbonization, a narrow, middle active combustion and also a narrow, upper oxidation zone were identified. The presence of basic instead of a mosaic anisotropy on the solids is indicative of weathering/oxidation prior to combustion. Air could circulate easily through open fractures within the uncompacted coal fragments, thus facilitating combustion at depth. The coal was carbonized at approximately 500-550°C at a rate of heating of 10°C/min. and subsequently combusted at 550-600°C. The coal has also been thermally altered to produce solid (semi-coke/coke), liquid (tar) and volatile matter. Different types of tar have been observed microscopically, interacting with coal fragments by briquetting them and acting as hydrogen donors to vitrinite.

Because additives such as coal-tar pitch often modify and change the optical texture and nature of residues during laboratory processes such as coal hydrogenation and co-carbonization, useful information can be gained by studying the natural coprocessing of coal with coal-tar pitch using optical microscopy and petrographic techniques.

INTRODUCTION

There have been numerous studies on the interaction between coals of different rank and additives containing oxygen, nitrogen, sulphur, aromatic compounds, petroleum pitches and coal-tar pitches (Marsh, 1973; Marsh et al., 1973a,b,c; Marsh et al., 1974; Marsh et al., 1980; Marsh and Neavel, 1980; Mochida et al., 1979a,b,c), and between coal macerals (Goodarzi, 1984). These additives often modify and change the optical texture and nature of residues during such processes as liquefaction (hydrogenation) and co-carbonization of coal macerals (Shibaoka et al., 1980; Goodarzi, 1984).

It has been shown by Shibaoka et al., (1980) and later by Steller (1981) that during hydrogenation the interaction between a coal and a hydrogen-rich additive results in the formation of reaction rims termed 'hydrogenation rims' These rims are possibly the precursors of vitroplast because they form from the interaction of additive with the vitrinite particles in the coal and are rich in

hydrogen. More recently, Gentzis and Goodarzi (1989) observed reaction rims formed around vitrinite particles due to the influence of carbonization by-products such as tar, in a self-burning coal wastepile in Coleman, Alberta, Canada.

Goodarzi (1984) reported similar reaction rims when highly reactive sporinite was co-carbonized with less reactive vitrinite in coals of the same rank. The reaction rims formed at the boundaries between carbonized vitrinite and sporinite had a distinct optical texture (size and anisotropy of the mosaic units). Goodarzi (1984) used coals from two different ranks (high-volatile bituminous C - % Ro = 0.62, and high-volatile bituminous A - % Ro = 1.04) and observed that the higher the rank of coal, the wider were the reaction rims. When the blend having the lower-reflecting vitrinite was carbonized, two types of optical texture were produced, an isotropic for vitrinite and a granular anisotropic for sporinite.

Three types of interactions may occur between a coal and an additive in a blend during carbonization which may result in the formation of different fluid phases. These are: fluid mixing, solvation and solvolysis (Mochida et al., 1979). During fluid mixing, the two miscible fluids forming from coal and additive create a new fluid with a new molecular composition and properties (Mochida et al., 1979). Solvation is considered to be more of a physical rather than a chemical process and involves the extraction or leaching of the coal by the additive, followed by a subsequent stabilization of the formed molecules in the fluid pitch additive. Solvolysis is a chemical process which involves simultaneous depolymerization and interaction of the coal and additive involving hydrogen transfer mechanism (Mochida et al., 1979).

This study deals with the interaction of organic components such as coal macerals and semicoke/coke fragments with tar generated by the self-burning of coal.

EXPERIMENTAL

A 440 cm deep channel was dug on the top of a self-burning coal wastepile at Coleman Collieries in Alberta and samples were taken from the oxidation (ash), combustion and carbonization zones as well as from unaltered coal. The hot samples were cooled in water immediately to prevent further oxidation and combustion.

The samples were then dried and crushed to pass -20 mesh (<850μm). They were subsequently polished and their maximum and minimum reflectances in oil (n_{oil} = 1.518) were measured using a Zeiss MPM II microscope, fitted with a Zonax microcomputer. Photomicrographs were taken under both plane-polarized light and with partially crossed polars.

RESULTS AND DISCUSSION

Gentzis and Goodarzi (1989) examined the organic petrology of the self-burning coal wastepile in Coleman, Alberta, Canada, (Figure 1a) and reported the reflectance profile of the different zones identified. These zones are: oxidation (ash), combustion and carbonization, all observed from top to base of the wastepile but their boundaries are not well defined (Figure 1b).

Carbonization zone

This zone is thick (~300 cm) and is subdivided into three subzones. The first subzone (B) is approximately 60 cm thick and consists mainly of warm, angular coal fragments. Two types of tar are observed (Figure 1c), an isotropic (% Romax = 1.07) and an anisotropic (% Romax = 2.35).

Subzone C is 180 cm thick and contains loose particles of hot, angular coal and semicoke/coke, becoming increasingly tarry towards the upper part. Three tar types are identified (Figure 1c), one is isotropic (% Romax = 0.72) and the other two are anisotropic (% Romax = 1.25 and 1.52 respectively) showing 'flow' texture.
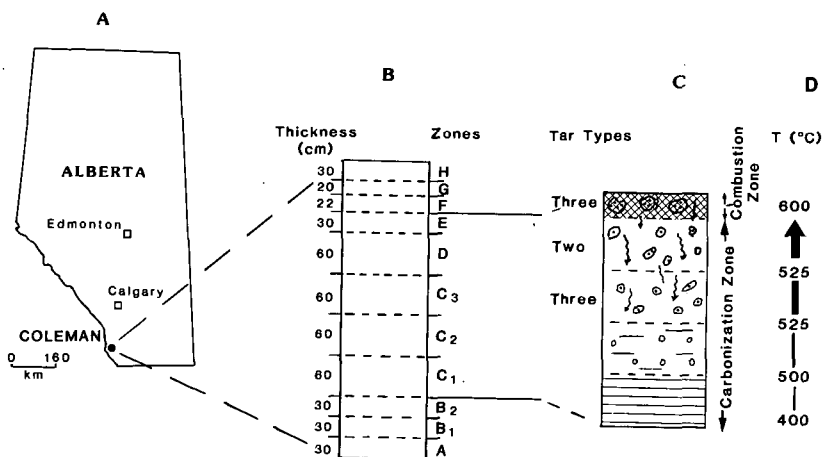

Figure 1 Location map of the coal wastepile in Coleman, Alberta (A), vertical profile of the self-burning coal wastepile showing different zones (B), types of tar (C) and temperature of their formation (D).

Subzone D is 60 cm thick consisting of angular semicoke and two tar types are present (Figure 1c). The isotropic tar has an Romax of 1.10%, while the anisotropic has an Romax of 1.66%.

Combustion zone

This zone is 30 cm thick and consists of a mixture of coke and ash. Both isotropic and anisotropic tars are present. The isotropic ones have an Romax of 0.86 and 1.13%, while the anisotropic ones have Romax values of 1.48, 1.90, 2.62 and 3.65% respectively. The high reflectance tar also shows granularity.

Oxidation (Ash) zone

The ash zone is 22 cm thick and consists of red ash and vents. Four types of tar are present, one isotropic (% Romax = 1.07) and three anisotropic (1.33, 1.53 and 1.77% Ro max respectively).

Heat generated by the combustion of coal alters the coal fragments in the oxidation zone and carbonization zone (Figure 1c) and produces solid residue (semicoke/coke), liquid (tar) and gases. The tar is mainly liquid to gaseous at the temperature of generation (500-550°C) but solidifies upon cooling and forms a pitch-like solid. The presence of the ash zone above the combustion zone in Coleman prevents the complete elimination of volatile by-products and, as a result, volatile matter escapes from vents developed at the side of the wastepile. These vents are impregnated by coal tar-pitch and often heat-affected fragments (semicoke/coke) are briquetted by tar (Gentzis and Goodarzi, 1989). Therefore, tar which formed due to coal devolatilization in the carbonization zone, such as in subzone C, migrates downwards in the wastepile due to force of gravity, penetrates the space among coal fragments and precipitates as isotropic to anisotropic by-products. The downward movement of tar is also due to a heat barrier produced by the combustion zone above (Figure 1b).

Similar observations were made by Goodarzi et al., (1988) on a partially combusted and coked bituminous coal seam from Aldridge Creek, British Columbia, Canada. A pitch-like, viscous material, which was soluble in chloroform-ethanol (87/13) azeotrope (similar to coal tar-pitch) formed from the carbonization of a medium-volatile bituminous coal seam (% Romax = 1.1), had migrated downwards filling the devolatilization vacuoles of the semicoke.

Figure 1c shows the various types of tar and their location in the wastepile and Figure 1d shows the temperature of their formation. Gentzis and Goodarzi, (1989) estimated that the coal was carbonized at a temperature of 500-550°C at a rate of heating of 10°C/min. and subsequently combusted at a higher temperature (550-600°C). The tar which formed in the semicoke subzone C_3 (~525°C) is isotropic, soft, typical of coal tar-pitch (Plate 1a). The coal rank in the Coleman section is medium-volatile bituminous (% Romax = 1.07), similar to the coal rank in Aldridge Creek. In both cases, coal was transformed to coke.

In Aldridge Creek, the coal seam is burning underground and under a sedimentary cover. As a result, the coal seam is directly transformed into carbonized residue. Therefore, no briquetting occurs but only impregnation of semicoke by tar takes place. In Coleman, coal is in fragmented form prior to burning, and is briquetted by tar-pitch as a result of self-burning. Most of the coke fragments in Coleman are subangular showing basic anisotropy, an indication that coal was probably weathered before being combusted (Goodarzi, et al., 1975).

Often, one or two waves of tar are observed filling cavities among semicoke fragments (Plate 1b). These two waves (types) of tar can be recognized on the basis of optical texture, an anisotropic, higher-reflecting tar which was

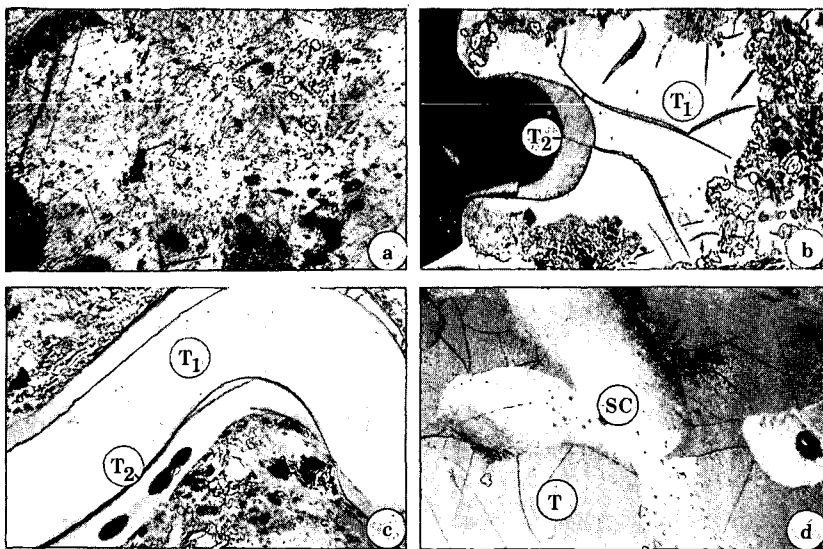obviously deposited initially, followed by an isotropic, lower-reflecting secondary tar.

PLATE 1

All photomicrographs taken in black and white, plane-polarized light, under oil immersion. Long axis is 240μm.
a) Isotropic and soft coal tar-pitch, semicoke subzone (C_3); b) Two waves of tar filling cavity in semicoke subzone (C_3). The initial tar (T_1) is higher reflecting, whereas the secondary tar (T_2) is isotropic; c) Two generations of tar showing fluidity; the older one (T_1) has a granular morphology and higher reflectance, the younger one (T_2) shows devolatilization vacuoles and lower reflectance; d) Semicoke fragments (SC) showing devolatilization vacuoles being surrounded by tar (T).

Tar also shows evidence of fluidity, an indication of its mobility. Plate 1c shows two types of tar, a higher-reflecting, slightly granular tar deposited initially and a secondary, lower-reflecting tar exhibiting devolatilization vacuoles. Both tars have infilled the crack between the semicoke fragments and have taken its shape. Occasionally, the subangular fragments of semicoke show devolatilization vacuoles and are completely surrounded by tar (Plate 1d). Within the semicoke subzone (C_3), mixing of semicoke and coal fragments may take place (Plate 2a-b) with tar binding both fragments. The low-reflecting tar is hydrogen-rich and apparently is able to react with the coal particles producing a distinct reaction rim (Plate 2a). This did not occur between the tar and semicoke fragments which show granular mosaic texture but no apparent reaction

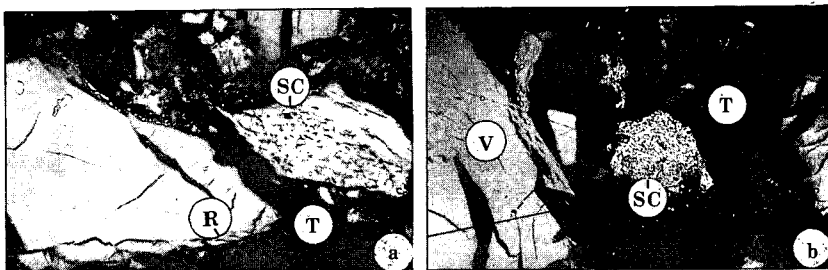1075

rim (Plate 2b).

PLATE 2 Conditions same as Plate 1.

a)   Low-reflecting, hydrogen-rich tar (T) reacting with coal and semicoke (SC) fragments.   Note the presence of a reaction rim (R) between coal and tar; b) Similar to 2a but there is no reaction rim formed due to the interaction of tar (T) and semicoke (SC). Vitrinite (V) also present showing desiccation cracks.

Often the cavities and cracks or surfaces of semicoke and coke fragments are lined by tar, indicating the passage of tar (Plate 3a-b). Tar within the pre-carbonization stage towards the base of the wastepile is often isotropic, soft and appears to have reacted with the coal fragments (Plate 4a). This tar is relatively hot and possibly acted not only as a binder but also as a hydrogen donor to vitrinite particles.   The briquetting of angular inertodetrinite fragments by tar is shown in Plate 4b. There is no apparent reaction between tar and inertodetrinite.
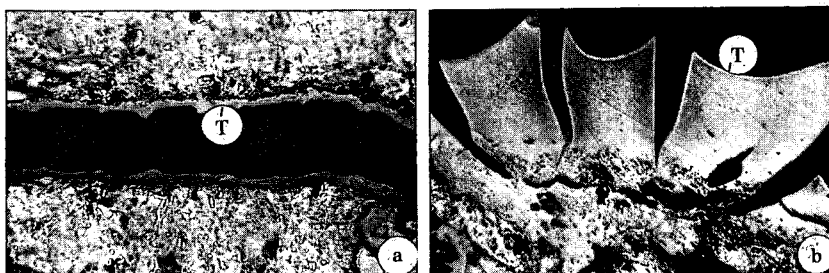

PLATE 3 Conditions same as Plate 1.

a)   The presence of thin lining of isotropic tar (T) indicating the passage of liquids and gases through semicoke fragments; b) The deposition of tar (T) in the cavity has lead to the formation of flower-like structures.

The morphology of the vitrinite fragments being briquetted by tar may give an indication as to the temperature of combustion. Usually rounded vitrinite fragments, as shown in Plate 4c, are indicative of higher temperatures as opposed to angular vitrinite fragments (Plate 4d) which indicate lower temperatures.
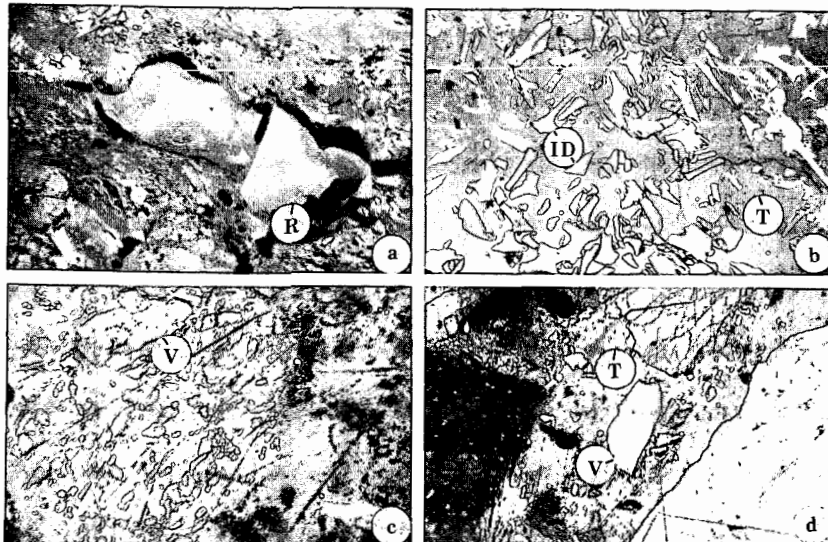

PLATE 4 Conditions same as Plate 1.

a) Tar reacting with coal fragments in pre-carbonization stage to form distinct reaction rims (R). The tar is hot and not only acts as a binder to briquette coal fragments but also as a hydrogen donor; b) Tar (T) is shown here briquetting angular inertodetrinite (ID); c) Tar briquetting rounded to semirounded vitrinite (V); d) Angular vitrinite (V) and inertinite being briquetted by tar (T).

CONCLUSION

The following conclusion can be drawn:

1) Tar generated from the combustion of coal may interact with coal and semicoke/coke fragments. Tar may not only act as a binder but also as a hydrogen donor to coal fragments, thus forming a distinct reaction rim.

2) Different tar types (primary and secondary) can be identified based on morphology, optical texture and reflectance.

3) Tar will briquette loose fragments of coal, as in the case of a wastepile but when coal is present in the form of a coherent seam, briquetting does

not take place but the coal is transformed into carbonized residue
impregnated by tar.

ACKNOWLEDGMENTS

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